

CRYSTALLOGRAPHIC AND MINERALOGICAL ASPECTS
OF SERPENTINE

Thesis submitted for the degree of Doctor of Philosophy in the Faculty
of Physical Sciences of the University of Oxford

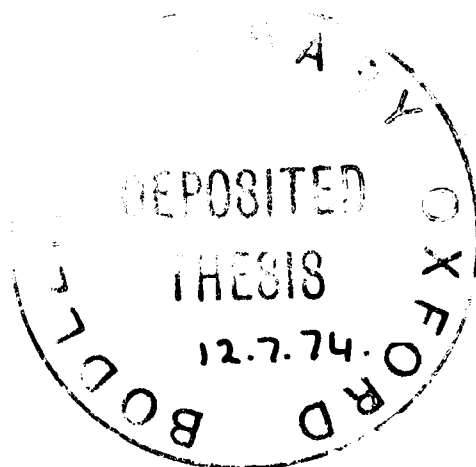
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March, 1974.

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ABSTRACT

Previous work concerning the structure of chrysotile is first reviewed, to provide a basis for discussion of the natures of two of the less common varieties of chrysotile - Povlen-type chrysotile and para-chrysotile. The results of x-ray diffraction, electron diffraction and electron-optical experiments on Povlen-type chrysotile are presented. On the basis of these observations a lath-like model for this material is rejected. In the course of discussion of the diffraction effects arising from Povlen-type chrysotile, the earlier theoretical treatment of the diffuse reflections of chrysotile is extended. In particular, the effects on the profiles of these reflections of a variety of distributions of fibril diameters within a fibre bundle have been investigated. The character of the reflections to be expected from chrysotile, based upon a high-order helical structure are described in the course of the evaluation of a possible helical model for Povlen-type chrysotile. This model is, however, rejected in favour of a polygonal model, which accounts satisfactorily for the observed diffraction effects. An explanation is offered for the "lumpiness" of the diffuse reflections apparent in some x-ray fibre photographs of chrysotile.

After a review of the few previous observations of para-chrysotile the results of electron-optical and electron diffraction studies are presented. An attempt is made to interpret these results in terms of a possible structural model for para-chrysotile. As in the case of Povlen-type chrysotile a lath-like model is rejected. Computations of the profiles of some of the diffuse reflections of para-chrysotile (based upon a cylindrical structure), which have not previously been published, are reported. In the light of the results of these calculations, which were carried out both for fibres consisting of bundles of fibrils exhibiting various distributions of diameters (applicable to x-ray diffraction) and for

the case of single fibrils of various diameters (applicable to electron diffraction), a cylindrical model is considered to be inadequate to explain the present diffraction results. It is suggested that a polygonal model, similar to that proposed for Povlen-type chrysotile, might be more appropriate.

Computer programs have been written to carry out the computation of the reflection profiles discussed in these two chapters, and are given in an Appendix.

In the succeeding chapters observations concerning several commonly occurring accessory minerals of serpentinites are reported. X-ray diffraction and electron diffraction studies of fibrous brucite are described. The intergrowth of brucite with chrysotile, particularly with para-chrysotile, is discussed in the light of the present observations in the electron microscope. The nature of 'nemalite' is discussed and a model, based upon intergrowth with chrysotile, is proposed to account for the published accounts of this material.

The structural and chemical characteristics of some of the hydroxycarbonate minerals are reviewed. The stability of brucite in the weathering environment and some chemical and crystallographic aspects of its alteration to various hydroxycarbonate-type minerals are considered.

Observations on the textural development of magnetite in serpentinites are reported. Some chemical data are presented, together with the results of an x-ray investigation into the structural orientation of fibrous magnetite intergrown with other minerals in cross-cutting veins.

Finally, an attempt is made to relate some of the observations reported in the present study to recent discussion of the processes involved in serpentinitisation.

ACKNOWLEDGMENTS

I should like to acknowledge the assistance of members of the technical staff of the Department of Geology and Mineralogy, Oxford, especially Mr. Philip Jackson for his help with the x-ray diffraction studies. For advice in the use of the electron microscope my thanks are due to Dr. D. Driver of the Clarendon Laboratory. I am grateful to Professor Zussman who gave permission for use of the electron microprobe in the Department of Geology, Manchester, and to Dr. F. Gibb who performed the analyses.

My thanks are due also to Mrs. Sheila Stanton for her care in typing the manuscript, to Mr. H. Tully who printed the photographs, to friends in Oxford for their assistance and to Mrs. Pat Moss for words of encouragement on numerous occasions. Most of all, however, I gratefully acknowledge the continued advice and encouragement of my supervisor, Dr. E.J.W. Whittaker. The N.E.R.C. provided financial support in the form of a post-graduate studentship.

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CHAPTER ONE

The classification of the serpentine minerals and the structure of chrysotile

1.1 Introduction

This chapter is intended to provide a background to the subsequent two chapters, in which the nature of two particular varieties of chrysotile will be discussed. It seems appropriate to consider first of all, the classification and general structural features of the serpentine minerals. The place of chrysotile within this classification will be considered, and the opportunity will be taken in this section (1.2) to comment briefly, on particular features of the structures of some of the minerals included in the serpentine group. A fuller discussion of the structure of chrysotile and the history of its elucidation will be given in section 1.3.

1.2 Classification of the serpentine minerals

The serpentine minerals can be classified as belonging to the kaolinite-serpentine group of the phyllosilicates*. They possess an asymmetric structure (compare for instance the chlorites, which can be described as symmetric), in that the layers are composed of one octahedral sheet and one tetrahedral sheet (see figure 1.1). In the octahedral sheet all of the available cation positions are occupied in the serpentines. Thus they can be further classified as trioctahedral 1:1 layer silicates, as distinct from the dioctahedral 1:1 layer silicates (e.g. kaolinite), in which only two thirds of the available octahedral cation sites are occupied.

The two sheets may be regarded as being linked through the apical oxygens of each tetrahedron, which replace two out of three of the hydroxyls in the plane of anions common to both sheets (figure 1.1). Throughout this paper the structure of serpentines is referred to in a manner which assumes that the octahedral sheet lies above the tetrahedral sheet. There is no particular reason for adopting this orientation, though it is customary in Western terminology.

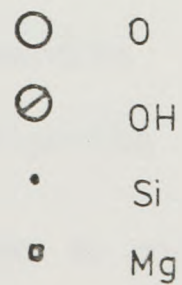
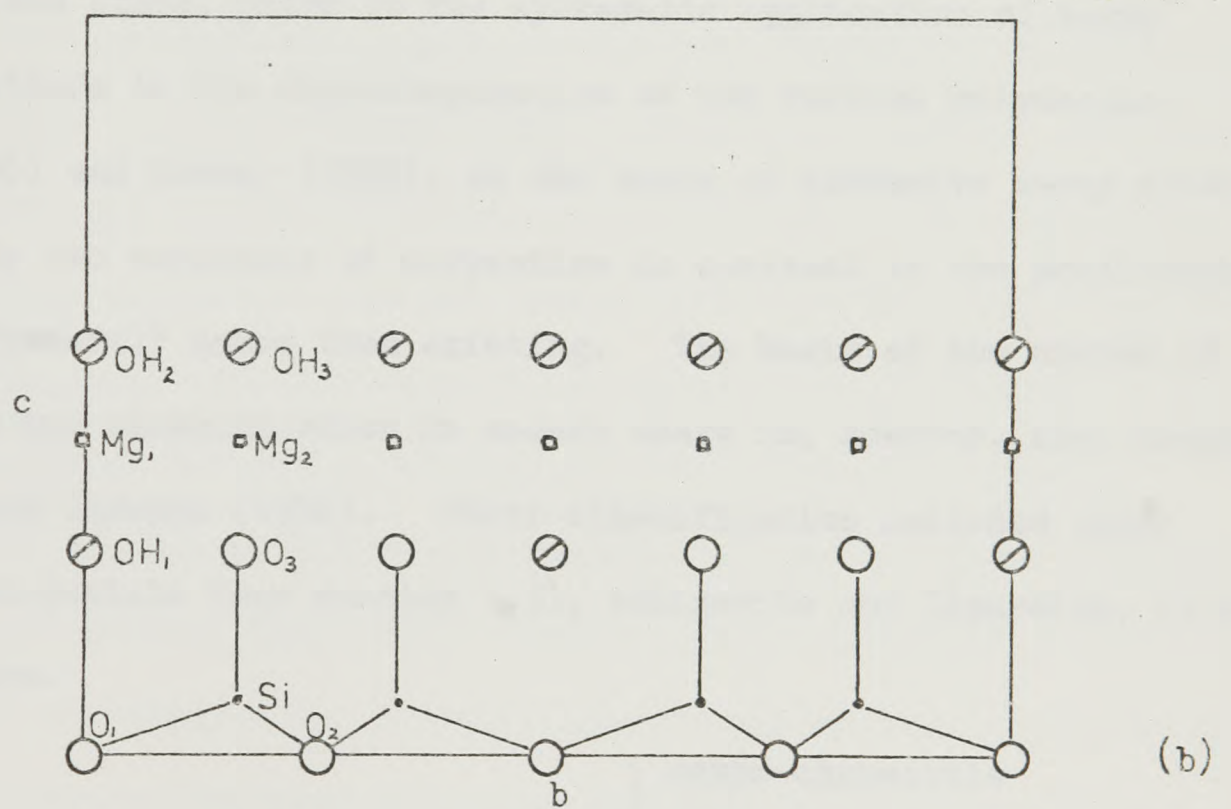
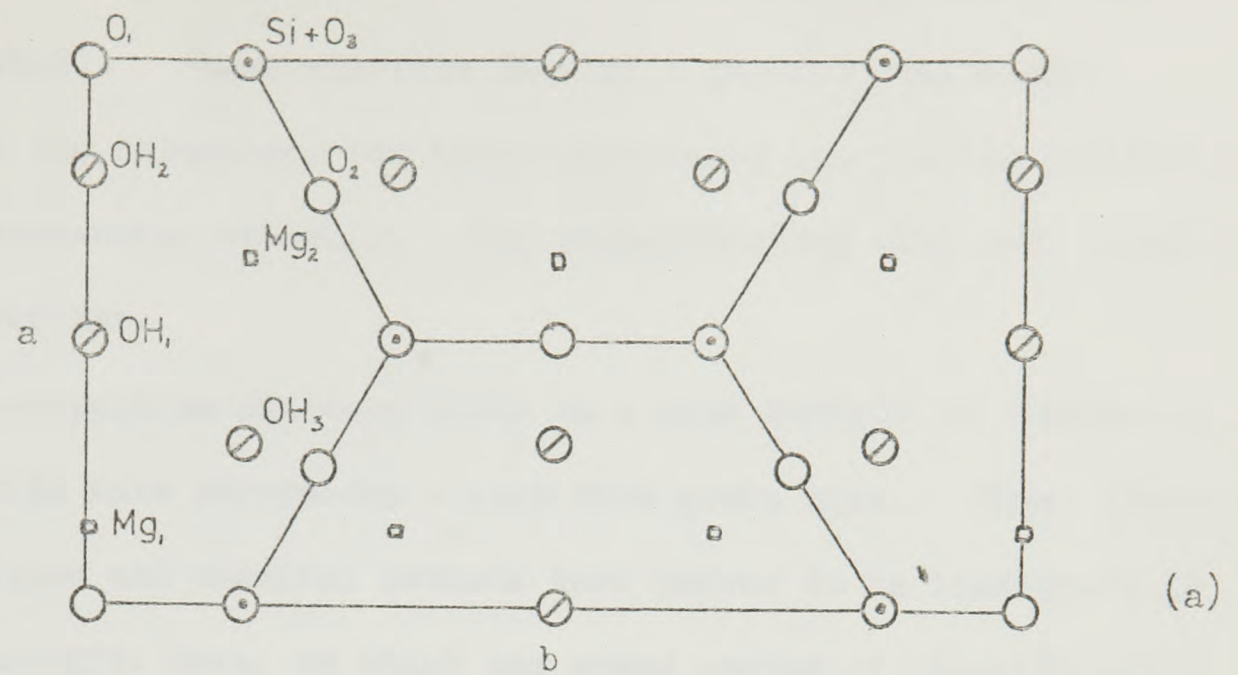


Figure 1.1. The structure of the chrysotile layer. (a) Plan view, (b) relationship of the octahedral and tetrahedral sheets, viewed along the a-axis. (After Whittaker 1956b, figure 3)

In addition to the serpentines, there exists a further group of trioctahedral 1:1 layer silicates, known as the septechlorites (Deer, Howie and Zussman, 1962). These minerals display a greater resemblance, chemically, to the chlorites, but their structures are closely related to those of the serpentine minerals. The septechlorites will not, however, be discussed further.

The serpentine minerals occur in a wide variety of textures, exhibiting - with rare exceptions - very fine grain size. Thus, classical optical techniques and chemical methods have proved to be inadequate in furnishing meaningful data, on which any sound system of classification might be based.

In consequence the nomenclature of the serpentine minerals was in a disorganised state, prior to the systematic application of x-ray diffraction methods to the characterisation of the various polymorphs. Selfridge (1936) and Gruner (1937), on the basis of extensive x-ray studies recognised only two varieties of serpentine in contrast to the proliferation of so-called "mineral" names then existing. The basis of the system of identification and classification in modern usage is, however, that proposed by Whittaker and Zussman (1956). Their classification included three varieties of chrysotile (see section 1.3), antigorite and lizardite, it is reproduced below.

		(ortho-chrysotile
		(
	(chrysotile	(clino-chrysotile
	(	(
serpentine	(lizardite	(para-chrysotile
	(	
	(antigorite	

Antigorite has been shown to possess a distorted layer structure, modulated in the a-axis direction in the form of an alternating wave (Zussman, 1954; Kunze, 1956, 1958), thus explaining the characteristic (though somewhat variable) superlattice parameter in the a-axis direction (43.4Å , Aruja, 1945). Fibrous antigorites, often termed picrolite, are elongated along the b-axis direction, and therefore give distinctive fibre

photographs indicating an axial repeat of $\sim 9.2 \text{ \AA}$

The name "lizardite" was proposed by Whittaker and Zussman (from the Lizard area of Cornwall, whence came several specimens of this variety of serpentine) for serpentine which did not show evidence of the large a-dimension of antigorite, but possessed an orthogonal structure, with $c \simeq 7.3 \text{ \AA}$ and which exhibited in its diffraction patterns evidence of varying degrees of three-dimensional order. Lizardite usually exhibits in the electron microscope a distinctive platy morphology (which may also be seen, though rarely, in hand specimen) and this has come to be recognised as a useful guide to its identification. The structure of lizardite was considered in more detail by Rucklidge and Zussman (1965) and by Krstanović (1968).

The recognition subsequently of the group known as the "six-layer ortho-serpentine" (Zussman, Brindley and Comer, 1957; Zussman and Brindley, 1957) led to a slight extension of the classification. The application of the term six-layer serpentine has not always been rigorous, and under this heading are frequently included multi-layer serpentines in general. The members of this group frequently display in their fibre diffraction photographs, the effects of disordered stacking of layers, making detailed structural interpretation (and hence classification) difficult. Most of the multi-layer serpentines do, in fact, seem to possess six-layer structures, which may, however, approximate two-layer or three-layer cells (Gillery, 1959).

A simple three-layer serpentine was reported by Coats (1968), while Jahanbagloo and Zoltai (1968) have reported a nine-layer ortho-serpentine. The latter may perhaps be better considered as a magnesium rich amesite rather than as a serpentine at all. Fairly extensive substitution by Al and Fe⁺⁺⁺ seems to be a characteristic feature of the multi-layer serpentines. These minerals occur but rarely as massive material making up the bulk of a serpentinite, being more usually found as veins. The multi-layer serpentines and lizardite may be polytypes, differing only in the type of stacking of

otherwise similar serpentine layers, though clearly the compositional relationships require to be understood more fully before this can be stated with any certainty.

Two somewhat unusual variants of serpentine may be mentioned, both of which display features which mark them apart from the 'normal' serpentine varieties. To one of these, which seems from its diffraction effects to possess a structure closely related to that of chrysotile, the term "Povlen-type chrysotile" has been applied (Krstanović and Pavlović, 1964). The nature of this material is discussed in chapter two.

The serpentine mineral from the Tilly Foster mine, New York State, described by Aumento (1967) is particularly unusual among the serpentines by virtue of its euhedral appearance in hand specimen. According to Aumento it "exhibits a strong platy habit, with a perfect cleavage parallel to (001)". Additional good cleavage directions lie parallel to (100) and (010) respectively and can, on occasion, give rise to 'cuboidal masses'. Aumento employed a variety of techniques during the course of his investigation, including various thermal methods, x-ray powder and single crystal methods and electron microscopy and diffraction. He concluded that the Tilly Foster material is an unstable serpentine polymorph which exhibits the combined properties of a number of other polymorphs. Aumento suggested that the unit cell was monoclinic and had a six-layer repeat, successive layers being related to each other by a relative displacement of $\pm a/3$ and $\pm b/3$ or by a rotation of 60° . Observation in the electron microscope led Aumento to postulate that the Tilly Foster serpentine is stable only in the macrocrystalline state and that when ground up mechanically (and viewed in the electron microscope) it tends to break down further, producing thin corrugated plates. These in turn give way to rods which subsequently curl to give chrysotile-like tubes.

Wicks (1969) has criticised certain features of Aumento's interpretation. In particular, his explanation of the 'rods' as precursors of the chrysotile-like tubes does not seem to be valid. This conclusion arises from consideration of the relative dimensions of the rods and tubes, taking into account the diffraction effects from the tubes. Rather it seems that the tubes should be considered as normal chrysotile fibrils. Further work on this strange material is clearly required before a wholly satisfactory appraisal of its nature can be made.

1.3 The structure of chrysotile

In this section an attempt is made to provide a review of the various investigations which had led to an appreciation of the nature of the structure of chrysotile. Detailed features of the structure are not in general discussed, but reference to some points is made during the course of chapter two.

It is now recognised that chrysotile has a cylindrical structure, correlating well with its very well developed fibrous habit. Pauling (1930a), writing before any attempt at a detailed structural analysis of chrysotile had been published, suggested that -

"The non-existence of a magnesium analogue of kaolinite is accounted for by the large values of the fundamental translations in the brucite layer ($a = 5.40 \text{ \AA}$), which would cause the kaolinite-type layer to curve."

Pauling (1930a), p. 578.

Chrysotile, in common with the other serpentine minerals (except in rare instances, lizardite) never occurs as what could be recognised as isolated single crystals, so that before the application of x-ray methods to the study of the serpentine minerals the axial ratios and crystal symmetry were unknown. The habit of the serpentine mineral from the Tilly

Foster mine is often such as to suggest the growth of macroscopic single crystals, but (as discussed above) the true nature of this material is far from clear.

Perhaps the earliest x-ray investigation to be reported was that of Anderson and Clark (1929)*. These workers examined fibre photographs of chrysotile (asbestos) samples from a wide variety of sources. Although the quantitative results given in this paper have proved to be of little value, one important finding (in the historical context) was the demonstration that the fibre repeat of chrysotile is close to that of amphiboles and diopside.

Warren and Bragg (1930) suggested that the structure of chrysotile was in fact related to that of amphiboles being based on Si_4O_{11} chains. They pointed out that the " Si_2O_5 " group (apparent when all the hydrogens are associated with oxygens as hydroxyl groups, and the formula is written in the now customary fashion $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) indicated a sheet structure analogous to the mica structures which had been recently described by Pauling (1930b). Nevertheless, on the basis of the physical properties, and the similarity of the fibre axis repeats in chrysotile and in amphiboles, they preferred a chain structure for chrysotile.

In later papers (Warren and Hering, 1941; Warren, 1942) the chain structure was, however, abandoned in favour of a structure involving disordered stacking of rather long, narrow sheets. In the latter of these two papers Warren gave unit cell parameters as follows -

$$a = 14.66 \text{ \AA}$$

$$b = 9.24 \text{ \AA}$$

$$c = 5.33 \text{ \AA}$$

$$B = 93^\circ 16'$$

with the c-axis as the fibre axis.

* Of historical interest is a paper published recently (Nitta, 1973) in which are reproduced two fibre diffraction photographs of asbestos, taken by Nishikawa and Ono in 1913. Both photographs were produced using the continuous spectrum from a platinum anti-cathode, one with the fibre perpendicular to the beam, the other with the fibre inclined.

The diffuseness of certain reflections was noted, and their appearance likened to cross-grating reflections from a two-dimensional lattice, and attributed to randomness in the stacking of layers.

Aruja (1943) reached essentially similar conclusions to those of Warren and his co-workers (see Whittaker 1956a, ch.2), explaining the anomaly that a mineral, so obviously fibrous as chrysotile, should be based on a sheet structure as being due to curvature of the layers, which limited their lateral growth. Thus Brindley (1951) wrote of chrysotile -

"... the silicate sheets have a ribbon-like form curved along the b-axis and probably containing only a small number of unit cells in this direction. The fibres grow along a, in which direction there is probably little or no curvature, . . ."

Brindley (1951) p.60

Whittaker (1951) demonstrated the existence of an orthorhombic variety of chrysotile, in addition to the more usual clino-chrysotile previously described. Padurow (1950) had suggested that chrysotile was in fact slightly triclinic, but this was repudiated by Whittaker (1952) and has never found a wide acceptance. In 1953 Jagodzinski and Bagchi noted the curvature of the layers in chrysotile, and made preliminary attempts to interpret the diffuse spots in the x-ray pattern in terms of varying radii of curvature. In the same year Whittaker (1953) published structure determinations of the orthorhombic and monoclinic varieties of chrysotile, based upon the assumption that "in so far as the diffraction pattern appears to resemble a single crystal rotation photograph it may be interpreted as such." (Whittaker (1954), p. 827). This investigation confirmed the earlier findings of Warren and Aruja that chrysotile can be regarded as the magnesium analogue of kaolinite and that the layers are curved.

This agreed well with early observations of chrysotile in the electron microscope (Turkevitch and Hillier, 1949; Bates, Sand and Mink, 1950; Noll and Kircher, 1950, 1951), which had suggested that chrysotile

might have a tubular structure. Observation of halloysite in the electron microscope had led Bates, Hildebrand and Swineford (1950) to suggest that halloysite, and probably chrysotile also might be tubular.

Not until the theory of diffraction by cylindrical lattices had been developed could the diffraction patterns from chrysotile be fully explained. The necessary theoretical background was provided independently by Jagodzinski and Kunze (1954 a, b, c) and by Whittaker (1954, 1955 a, b, c). The former authors developed the diffraction theory with particular reference to the structure of chrysotile, while Whittaker adopted a slightly different approach and considered the problem in a more general form. He investigated the concept of a cylindrical lattice and presented a classification of cylindrical lattice types (Whittaker, 1955 d), see Table 1.1.

Whittaker made certain assumptions concerning the types of cylindrical lattice which would be likely to occur in real structures, in particular those that would be capable of producing a tubular morphology. He therefore "considered in detail only those lattices whose right sections are sets of equally spaced circles, or the successive turns of the involute of a circle." - Whittaker (1955 d), p.571. The latter can conveniently be referred to as spiral lattices, the former as cylindrical (or circular) lattices.

Diffraction theory was developed by Whittaker for the cylindrical lattice types, but mathematical analysis of the spiral lattice types proved to be intractable (Whittaker (1956 a), p.168) and was abandoned, in favour of a more indirect treatment by optical diffraction experiments (Whittaker, 1955 b). Incomplete cylindrical lattices were also investigated by Whittaker in this manner, the results being reported in the same publication.

At this stage the diffraction effects from chrysotile could be interpreted in terms of the appropriate diffraction theory. Structure

TABLE 1.1

Types of Cylindrical Lattice*

	Kind	Inter-axial angles	Orientation of b-axis to right section	Circular	Spiral
Anorthic	(1st)	$\alpha \neq \beta \neq \frac{1}{2}\pi$	(Parallel	R	-
	(2nd)		(Inclined	H	H
Monoclinic	(1st	$\beta \neq \alpha = \frac{1}{2}\pi$	Parallel	R	-
	(2nd	$\alpha \neq \beta = \frac{1}{2}\pi$	Parallel	R	R
	(3rd	$\beta \neq \alpha = \frac{1}{2}\pi$	Inclined	H	H
	(4th	$\alpha \neq \beta = \frac{1}{2}\pi$	Inclined	H	-
Orthorhombic	(1st)	$\alpha = \beta = \frac{1}{2}\pi$	(Parallel	R	R
	(2nd)		(Inclined	H	-

The letters H and R denote the existence of a lattice in the helical or regular series respectively

* from Whittaker (1955d, Table 1).

determinations were carried out by Whittaker on clino-chrysotile (1956b) and on ortho-chrysotile (1956c). The structure of para-chrysotile - the minor constituent responsible for subsidiary layer lines on many fibre photographs, and with a spacing indicating an axial repeat of $\sim 9.2 \text{ \AA}$ - was also interpreted in terms of the cylindrical lattice concept (1956d). The characterisation of para-chrysotile completed the three-fold classification of chrysotile. Cell parameters of these three polymorphs, together with those of some other serpentine minerals, are given in Table 1.2.

Para-chrysotile is easily distinguished from the other chrysotiles by virtue of being curved about the b-axis rather than the a-axis; its structure is discussed further in chapter three.

The diffuse reflections arising from chrysotile were treated in a separate paper (Whittaker, 1957). The successful interpretation of the fibre diffraction patterns from chrysotile, in terms of a cylindrical structure now awaited final confirmation by direct observation, in the electron microscope, of cylindrically arranged layers. The early observations had not provided indisputable evidence for a cylindrical structure, and evidence in direct conflict with such a structure was adduced from density measurements on blocks of chrysotile - most notably by Pundsack (1956). A full discussion of the problems raised by the various density determinations would involve digression; the implications and various solutions suggested have been discussed by Whittaker and Zussman (1971).

Bates (1958) - see Whittaker and Zussman, 1971 - Bates and Comer (1959) published evidence supporting a tubular morphology, and in 1960 Maser, Rice and Klug published the first electron micrographs of transverse sections of chrysotile.

Previous observations of fibres in cross-section had been limited to synthetic samples in which the fibres were considerably shorter than those naturally occurring and therefore more likely to lie on the microscope grid

TABLE 1.2

Cell parameters of some serpentine minerals

Mineral Name	a (Å)	b (Å)	c sin B (Å)	β	Reference
Ortho-chrysotile	5.34 ± 0.01	9.2	14.63 ± 0.01	90°	Whittaker, 1956c
Clino-chrysotile	5.34 ± 0.01	9.2	14.63 ± 0.01	93° 16'	Whittaker, 1956b
Para-chrysotile	5.3	9.2 ± 0.02	14.7 ± 0.01	90°	Whittaker, 1956d
Antigorite	43.5*	9.26	7.28	91° 24'	Aruja, 1945
Lizardite	5.31	9.20	7.31	90°	Rucklidge & Zussman, 1965
3-layer serpentine	5.346	9.205	21.930	90°	Coats, 1968
6-layer serpentine	5.322	9.219	43.59	90°	Zussman & Brindley, 1957
Tilly Foster serpentine	5.32	9.22	7.28	93.3°	Aumento, 1967

* a cell dimensions of antigorite varying from 16-110 Å have been reported from electron diffraction experiments. (Chapman and Zussman, 1959).

in such a way as to present an end-on view. Apart from these observations only the broken ends of what appeared to be tubes had been seen, altogether a numerically small and, it might be argued, unrepresentative sample. Maser et al used an embedding technique and ultra-microtomy in the preparation of their sections, adapting methods used in the preparation of biological specimens.

A similar method of preparation was used by Yada (1967) who published micrographs of exceptional quality. The resolution was such that the lattice fringes corresponding to individual layers are resolved, clearly revealing spiral growth, with single-layer and multi-layer spirals. In a later paper Yada (1971) published electron micrographs of fibrils which show evidence of both spiral and concentric growth of layers. In addition, Yada presented evidence of two or three-stage growth of fibrils, in a specimen from Tasmania. Several of Yada's micrographs, illustrating some of the growth patterns observed, are reproduced in figure 1.2.

It should perhaps be borne in mind that all the observations of chrysotile in the electron microscope are subject to the criticism that some of the features observed may be artefacts of the preparation process. Even taking such considerations into account, it seems that the electron micrographs demonstrate convincingly the correctness of the interpretation of chrysotile in terms of a cylindrical structure.

Observation in the electron microscope has the advantage (as compared with x-ray diffraction) that it provides the opportunity to observe the diffraction effects due to single fibrils, in particular the possibility of observing the diffraction pattern of isolated para-chrysotile (see chapter three), which is unlikely to be achieved in x-ray diffraction of fibre bundles.

Moreover, electron diffraction techniques permit the observation of special effects which arise from the cylindrical structure and can be

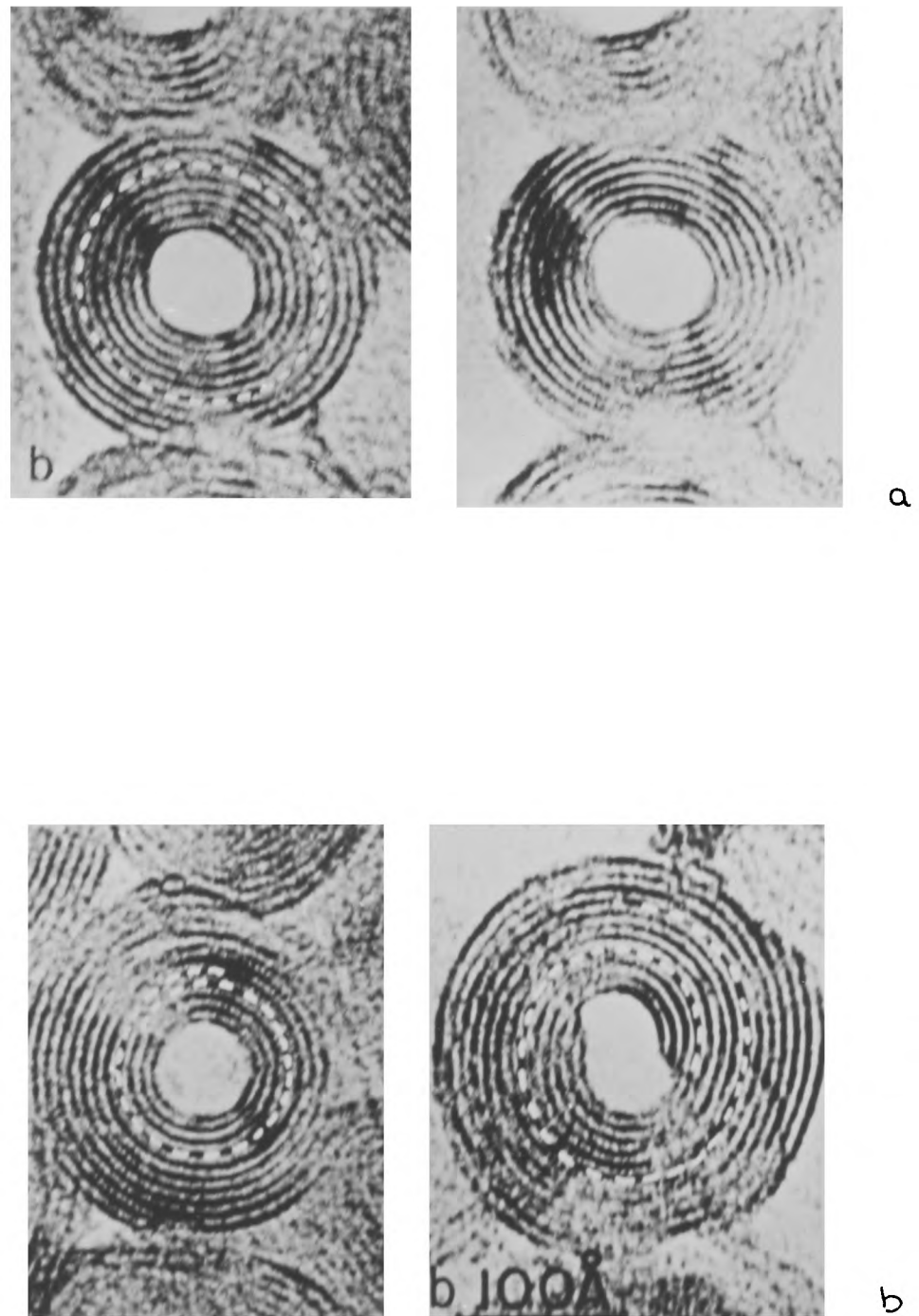


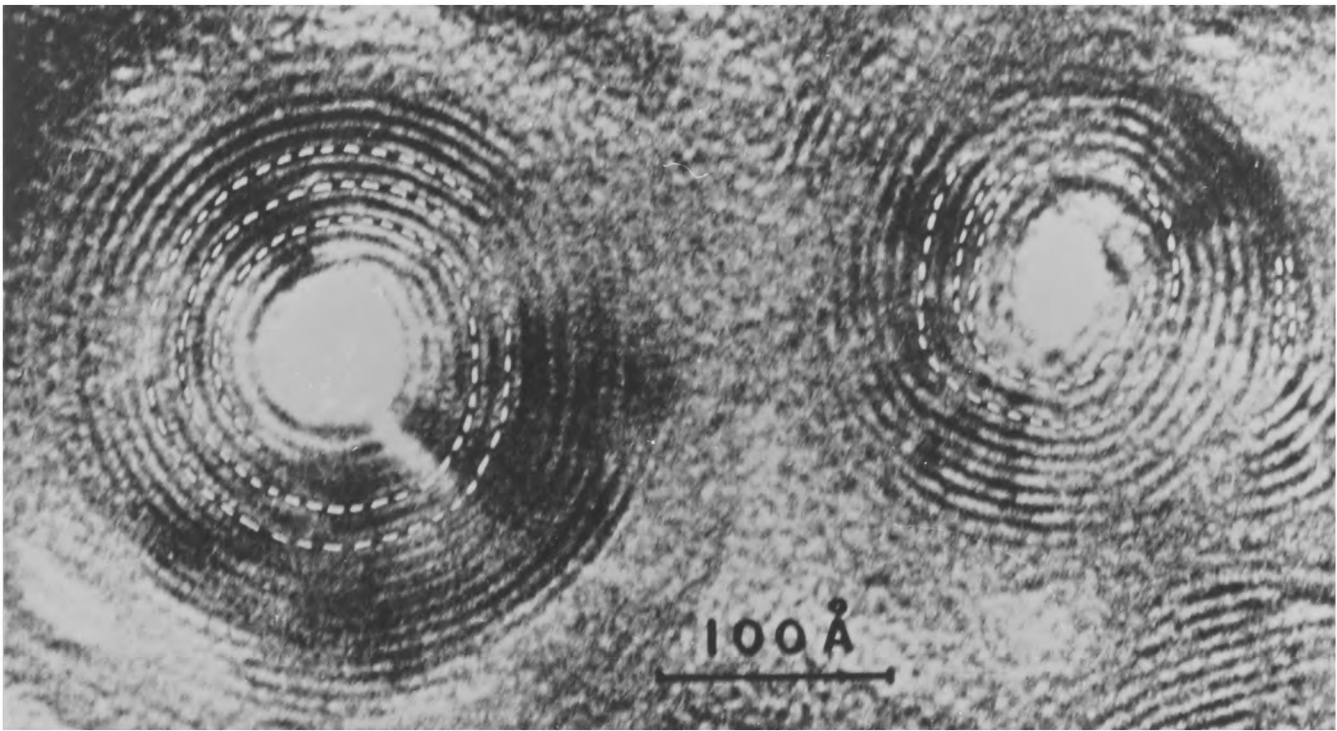
Figure 1.2. Some growth habits of chrysotile

a)concentric growth (Yada 1971, fig.14)

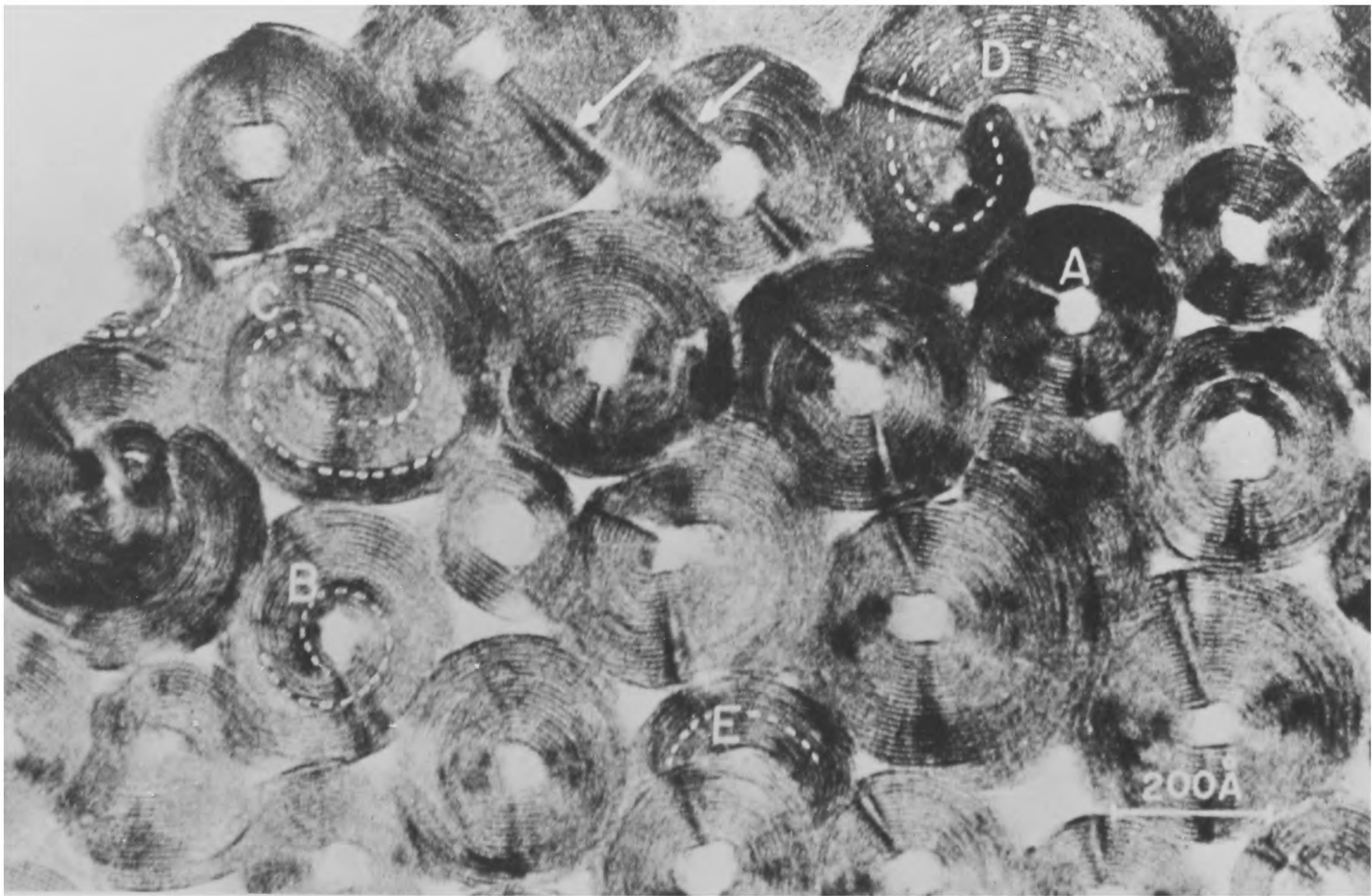
b)spiral growth (Yada 1971, fig.13)

c)double start spiral growth (Yada 1967,fig.9)

d)a variety of growth patterns (Yada 1971, fig. 12)



c



d

obtained only from single fibrils; in the x-ray case those effects are blurred out by the superposition of randomly different effects from the many fibrils at different azimuths in the fibre bundle. "Fine-structure" effects occurring in both sharp and diffuse reflections - though arising from different causes in the two instances - are discussed by Whittaker and Zussman (1971).

The first demonstration of fine structure in the diffuse (cross-grating type) reflections arising from a cylindrical structure was by Honjo and Mihama (1954), who observed the effect in halloysite. Fine structure in the sharp reflections of chrysotile though predicted in the course of the early theoretical work, by Whittaker (1954) was not observed until 1963 (Whittaker, 1963).

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CHAPTER TWO

The nature of Povlen-type chrysotile

2.1 Introduction

Diffraction effects similar to those which are here interpreted as being characteristic of Povlen-type chrysotiles, were reported as early as 1956 by Ekhardt. He discussed the nature of "schweizerite", which had been included in the chrysotile group by Selfridge (1936), and published an x-ray fibre diagram (his figure 1, page 33). Eckhardt stated that this material was chemically and optically identical with other chrysotiles but that the fibres were more brittle and tended to be platy. Zussman, Brindley and Comer (1957, figure 1d, page 138) published the results of electron diffraction of a "splintery clino-chrysotile" from Zermatt*. The electron diffraction pattern suggests that this material was in fact a Povlen-type clino-chrysotile. Zvyagin (1967, figure 53) published an electron diffraction pattern, from a "tubular particle", which is similar to the pattern from splintery clino-chrysotile referred to above. No comment was made, however, by Zvyagin, concerning the differences between this pattern and those normally obtained from chrysotile fibrils.

The term "Povlen-type clino-chrysotile" was introduced by Krstanovic and Pavlovic (1964) and was applied to a group of clino-chrysotile specimens (identified as such from their powder patterns) which showed unusual fibre patterns in x-ray diffraction. Further examples of Povlen-type chrysotile were reported by Krstanovic and Pavlovic in 1967. In neither paper, however, did they discuss the characteristic features of the diffraction patterns from Povlen-type chrysotiles in any great detail.

* It seems that this specimen had been identified as "schweizerite"; see below.

TABLE 2.1

Positions of schweizerite reflections
and the indices assigned to them by
Eckhardt (1956, Table 1)

Layer line	Position		Intensity	Indices
	1	2		
Zero	0.0108	0.135	s	001
	0.0257	0.208	s	020
	0.0436	0.271	vs	002
	0.0984	0.407	s	003
	0.1757	0.544	m	004
	0.2499	0.649	vs	060
	0.2743	0.679	m	005
	0.3973	0.818	m	006
	0.7069	1.091	m	008/0.10.0
First	0.0285	0.115	s	110
	0.0875	0.335	s	130
	0.0982	0.361	s	13 $\bar{1}$
	0.1147	0.398	m	113
	0.1337	0.437	m	13 $\bar{2}$
	0.1740	0.508	w	13 $\bar{3}$
	0.1949	0.542	s	150
	0.5976	0.985	s	190

1. values of $\sin^2 \theta$ given by Eckhardt
2. values of ξ ($\text{\AA}^{-1}$) calculated from 1

Cell parameters - $a = 5.37 \pm 0.04 \text{ \AA}$
 $b = 9.22 \pm 0.08 \text{ \AA}$
 $c = 7.40 \pm 0.07 \text{ \AA}$
 $\beta = 93.2^\circ$

Film taken with $\text{CuK}\alpha$ radiation

Ekhardt (1956) indexed the fibre patterns of "schweizerite" on the basis of a single-layer monoclinic cell (see Table 2.1) and assigned hkl type indices (in addition to 1k0 type indices) to reflections on the first layer line. Zussman et al (1957) stated that reflections on the zero and even layer lines of the pattern from the splintery chrysotile were similar to those in diffraction patterns from silky chrysotiles, but that on odd order layer lines the hk0 bands were weaker and several spots of type 131 were present.

Krstanović and Pavlović (1964) distinguished Povlen-type clino-chrysotiles on the basis that their x-ray fibre patterns* showed "sharp reflections on all layer lines up to the sixth" - as distinct from normal chrysotiles, which give sharp reflections only on even order layer lines. They did not, however, show a fibre diagram in any of their figures, but mentioned the presence of reflections of medium intensity on even layer lines with $l = \text{odd}$, as did Zussman et al, indicating a two-layer cell.

Powder data were presented by Krstanović and Pavlović (1964) but the only extra reflection given in their data - as compared with normal clino-chrysotile (Whittaker and Zussman, 1956, Table II) - is at 2.604 Å, indexed as 131. This additional reflection is again the only extra reflection present in the powder data published by these workers in 1967 (Table 1, columns 11, 12). In this later paper, devoted primarily to a discussion of six-layer serpentines they show partly indexed fibre diagrams (their figure 1a, b, c; reproduced as figure 2.1a, b, c) in schematic form for Povlen-type clino-chrysotile (figure (a)), for six-layer orthoserpentine (b) and for a mixture (or intergrowth) of the two (c). Some confusion seems to have arisen in the preparation of this figure: the indexing of the second layer reflections of (b) conforms to a six-layer orthoserpentine, but the zero layer, stated in the text to contain extra 0kl reflections is quite normal. On the other hand the zero layer of diagram (a) stated to be Povlen-type clino-chrysotile

* recorded using the technique described by Whittaker (1953a).

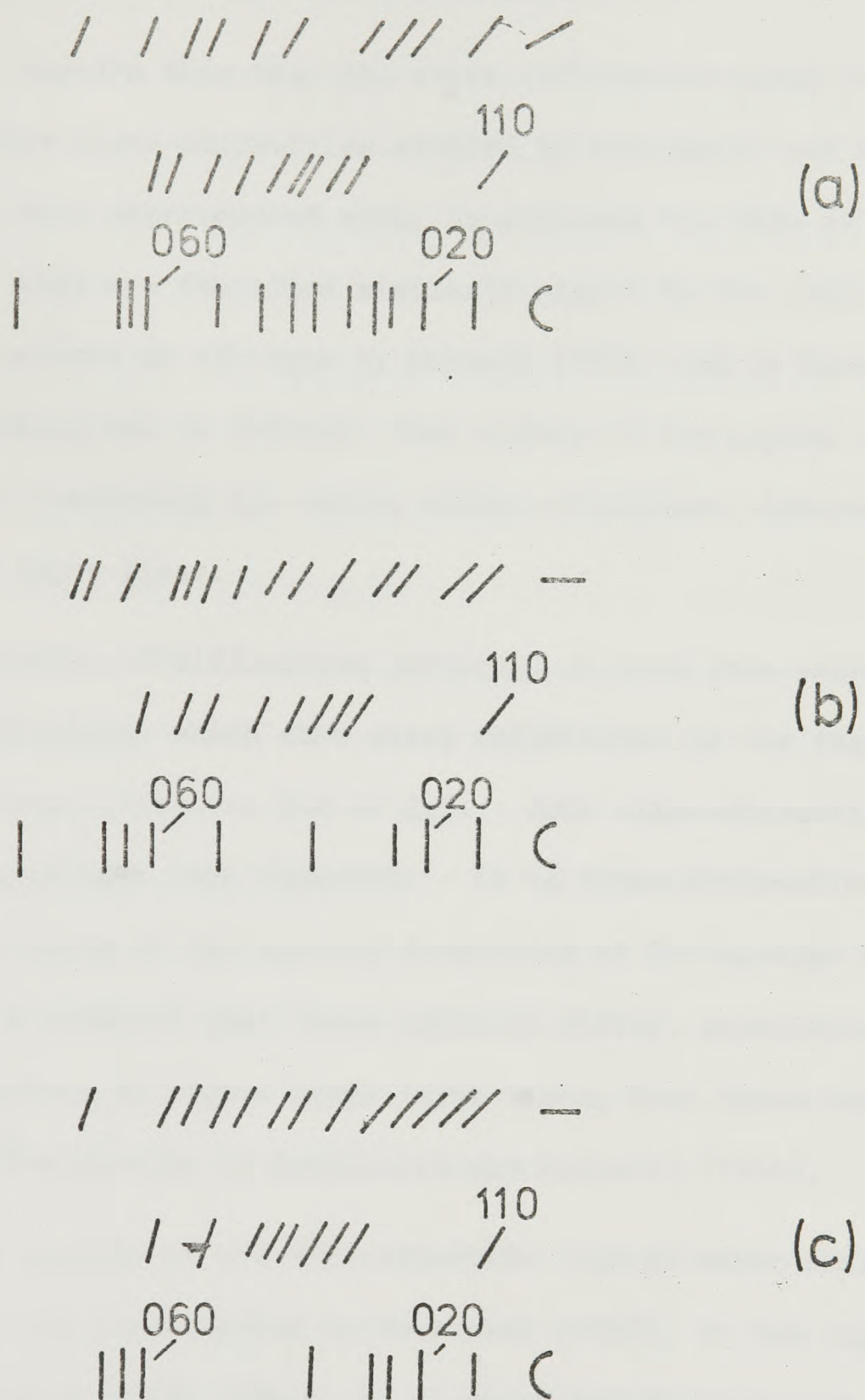


Figure 2.1. Diagram illustrating fibre photographs of (a) Povlen-type chrysotile, (b) six-layer ortho-serpentine and (c) a mixture of the two in approximately equal proportions. (Arstanović and Pavlović 1967, figures 1 a,b,c). See text for discussion.

does show a series of extra reflections following 020. In all three diagrams the tails following 110 - together with any sharp reflections there may be in this region - is omitted. From the powder data it seems that while the six-layer orthoserpentine give a series of 111 type reflections, the Povlen-type specimens do not.

It appears then that the extra reflections which characterised the Povlen-type clino-chrysotiles studied by Krstanović and Pavlović (1964, 1967) were superimposed upon, or replaced the tail of the 130 reflection; they are therefore similarly placed to the extra, sharp reflections indexed as 131 type by Ekhardt (1956) and by Zussman et al (1957). Nothing can be deduced, from either of the papers (by Krstanović and Pavlović) concerning the extra, sharp reflections observed on the higher order layer lines.

Examples of diffraction patterns, derived from both x-ray and electron diffraction, which show sharp reflections in the region of the tail of 130 are given in figures 2.2 to 2.5. Both clino-chrysotile and ortho-chrysotile types have been observed. It is these diffraction patterns which will form the basis of the ensuing discussion of Povlen-type chrysotiles, although it is possible that these patterns differ, particularly in respect of the reflections on higher order layer lines, from those originally described as Povlen-type by Krstanović and Pavlović (1964).

The profile of the 130 reflection (and of other diffuse reflections) of chrysotile was investigated by Whittaker (1957), in the light of earlier studies (Whittaker 1953b, 1956 a, b, c) which had demonstrated the cylindrical structure of chrysotile. It was shown that a diffuse, but intense secondary maximum is an essential feature of the profile of this reflection, and that it arises from the structure of the chrysotile layer, even though each layer in the fibre diffracts independently. This large "hump", had been attributed by Aruja (1943) to an unresolved combination of 132 and $1\bar{3}2$, while smaller

subsidiary maxima were assigned by him, indices of types $13l$ and $13\bar{l}$. Such indices are meaningless, however, in the context of a cylindrical structure, with its inevitable azimuthal disorder between layers.

A further type of 'structure' within the tail regions of the diffuse $hk0$ reflections arises from the cylindrical structure of chrysotile. This fine-structure which can only be observed in electron diffraction, when the diffraction effects arising from single fibrils can be obtained, has been discussed by Whittaker and Zussman (1971)*. It is quite different in character from the electron diffraction effects given by Povlen-type chrysotiles. Moreover, in an x-ray experiment when the diffraction effects arise from a very large number of fibrils with random azimuth such fibre structure is blurred out, to give a smooth profile.

Both Zussman et al (1957) and Krstanović and Pavlović (1964, 1967) sought to justify their $13l$ type indices (which imply a degree of ordering in the b-axis direction - a feature incompatible with a cylindrical structure) for the extra reflections of the first layer line. They suggested that Povlen-type chrysotile is based not on a cylindrical structure, but rather that it is fundamentally lath-like. Some support for this exists in the morphological observations, made by both groups, in the electron microscope. In particular, Zussman et al reported that "electron micrographs show mainly elongated laths of widths ranging up to about $2000 \text{ \AA}$ ".

Ekhardt (1956) suggested that "schweizerite" did not possess a cylindrical structure, although he deduced from his x-ray investigations that it consisted of fibre bundles. Ekhardt's macroscopic morphological observations indicated a platy habit but from his paper it seems that he did not relate this feature (and its possible implications regarding the fundamental structure of the material) to the presence of reflections with hkl type indices.

The conclusion that Povlen-type chrysotiles are fundamentally lath-like leaves a problem, however, concerning the orientation of material

* see also Chapter 1.

within the laths. Both the x-ray fibre photographs and the electron diffraction patterns of apparently single fibrils, of Povlen-type chrysotiles show rotational symmetry about the fibre axis. This is clearly demonstrated by the presence of both 00l and 0k0 type reflections on the zero layer line. Fibrous minerals, for instance amphiboles, which appear to be lath-like in electron micrographs commonly give x-ray fibre photographs showing full rotational symmetry. But, electron diffraction patterns of individual laths correspond to sections of a normal reciprocal lattice.

The rotational symmetry of the electron diffraction patterns of Povlen-type chrysotiles implies that there is a large number of units within a lath having a common a-axis, but which are in many orientations about that axis. For a lath $< 2000 \text{ \AA}$ across it is difficult to imagine how the units are arranged within the lath. In the case of the fibre of Povlen-type ortho-chrysotile shown in figure 2.4 which is approximately $700 \text{ \AA}$ in diameter, it is inconceivable that the fibre is not based on some structure possessing a degree of rotational symmetry about the a-axis. A further feature which suggests that the structure of Povlen-type chrysotiles is more akin to cylindrical chrysotile than to a lizardite type of layered structure, is the deficiency in hkl type reflections and the presence of diffuse reflections, particularly on the odd order layer lines.

2.2 Present observations of Povlen-type chrysotiles

During the present investigation the diffraction effects from a number of specimens, of more or less splintery fibres (as distinct from silky (asbestos) chrysotile), have been observed. All but two of these have been of Povlen-type clino-chrysotiles, several examples of which were kindly supplied by Dr. F.J. Wicks of the Royal Ontario Museum. Further examples of Povlen-type clino-chrysotile were afforded by examination of material, labelled "Schweizerite", in the Oxford University Museum Collection (by courtesy of Dr. F.B. Atkins). These samples, from localities near Zermatt, include the

TABLE 2.2a

Positions and proposed indices of Povlen-type
ortho-chrysotile reflections observed in x-ray
and electron diffraction

Layer line	x-ray diffraction*		electron diffraction	
	($\text{\AA}^{-1}$)	I	($\text{\AA}^{-1}$)	Proposed indices
Zero	0.14	vs	0.14	002
	0.22	s	0.22	020
	0.28	vs	0.28	004
	0.41	w		x
	0.42	m	0.41	006
	0.55	w		x
	0.56	m	0.55	008
	0.65	vs	0.65	060
	0.68	vw		x
	0.69	w	0.69	0.0.10
	0.81	vw		x
	0.82	mw	0.83	0.0.12
	0.95	vw		x
	0.96	w	0.97	0.0.14
	1.09	w		0.0.16
First	0.09	s	0.11	110
	0.32	s	0.33	130
	0.35	vs	0.35	132
	0.38	s	0.38	133
	0.42	ms	0.42	134
	0.47	vs	0.47	135
	0.52	ms	0.52	136
	0.54	w		150
	0.58	s	0.58	137
	0.63	s	0.64	138
	0.70	ms	0.70	139
	0.76	m	0.76	1.3.10
	0.78	vw		170
	0.82	w		1.3.11
	0.88	vw		1.3.12
	0.98	mw		190

TABLE 2.2a (Contd.)

Layer line	x-ray diffraction		electron diffraction	
	($\text{\AA}^{-1}$)	I	($\text{\AA}^{-1}$)	Proposed indices
Second	0	vs	0.06,0.13	201, 202
	0.20	s	0.20	203
	0.27	ms	0.27	204
	0.34	s	0.34	205
	0.41	mw	0.41	206
	0.48	m	0.48	207
	0.55	mw	0.55	208
	0.62	w	0.62	209
	0.64	w		260, 261
	0.66	ms	0.65	262
	0.67	vw		263
	0.69	vw	0.69	2.0.10
	0.73	vw	0.72	265
	0.75	vw		2.0.11
	0.77	vw	0.76	266
	0.80	vw	0.81	267
	0.85	vw		268
	0.90	vw		2.0.13
Third	reflections above		0.08	310
	the second layer		0.31	330
	line not observed		0.34	332
	on fibre photo-		0.42	334
	graphs taken with		0.64	338
	CuK radiation.		0.77	3.3.10
			0.89	3.3.12

Indices assigned on the basis of an orthorhombic unit cell - $a = 5.34 \text{ \AA}$
 $b = 9.24 \text{ \AA}$
 $c = 14.63 \text{ \AA}$

* Specimen 8/20F, data from fibre photographs taken in 6 cm diameter camera, with CuK $_{\alpha}$ radiation.

X "extra" reflections referred to in section 2.2

TABLE 2.2b

Positions and proposed indices of Povlen-
type clino-chrysotile reflections observed
in x-ray diffraction

Layer line	x-ray diffraction*		Proposed indices
	($\text{\AA}^{-1}$)	I	
Zero	identical to Povlen-type ortho-chrysotile, except for the absence of the "extra" reflections, marked (X)		
First	0.10	vs	110
	0.33	s	130
	0.36	vs	132
	0.40	mw	133
	0.44	m	134
	0.55	m	150
	0.99	mw	190
Second	0	mw	200
	0.12	m	20 $\bar{2}$
	0.16	vs	202
	0.23	vw	203
	0.25	vw	20 $\bar{4}$
	0.29	m	204
	0.37	vvw	205
	0.40	vw	20 $\bar{6}$
	0.43	m	206
	0.53	m	20 $\bar{8}$
	0.57	w	208
	0.65	ms	260
	0.70	vvw	2.0.10

Indices assigned on the basis of monoclinic unit cell - $a = 5.34 \text{ \AA}$
 $b = 9.24 \text{ \AA}$
 $c = 14.63 \text{ \AA}$
 $B = 93^{\circ} 16'$

* Specimen G148; fibre photograph taken with CuK_{α} radiation.

specimen from the Findeten Glacier (No. 9652)* examined by Zussman et al (1957), and referred to above.

The Povlen-type ortho-chrysotile specimen (No. 8/20F) was from the serpentine collection of the Department of Geology and Mineralogy, Oxford. Brief descriptions of the specimens whose diffraction effects have been observed, together with their identifying numbers and source, are given in Appendix B.

The fibre photograph reproduced in figure 2.2 is of a splintery serpentine mineral (from specimen No. 8/20F), identifiable from its powder pattern as ortho-chrysotile. It shows the sharp reflections on the first layer line which are taken to be characteristic of Povlen-type chrysotiles. All reflections on the photograph show the effects of misorientation, but a notable feature is the arcs linking reflections on the first and second layer lines. The latter are normal 20l type reflections, to be expected from a two-layer ortho-chrysotile.

On this photograph a series of weak reflections, just resolved from the normal basal (00l) reflections, can be distinguished. They suggest the presence of material having a basal spacing somewhat greater than that of chrysotile ($14.8 \text{ \AA}$ as compared with $14.6 \text{ \AA}$). In addition there are extra reflections to the high angle side of the normal 060 reflection. None of those extra reflections was, however, observed in electron diffraction. Similar extra reflections were observed on the zero layer line of one photograph of Povlen-type clino-chrysotile (No. G632).

The significance of these spots is not known, but since their presence seems not to be an essential feature of Povlen-type chrysotile they have been excluded from further consideration. The co-ordinates of these reflections, together with those of the other reflections observed on fibre photographs of Povlen-type ortho- and clino-chrysotile, are given in Table 2.2.

* The numbers in parentheses refer to the specimens listed in Appendix B.

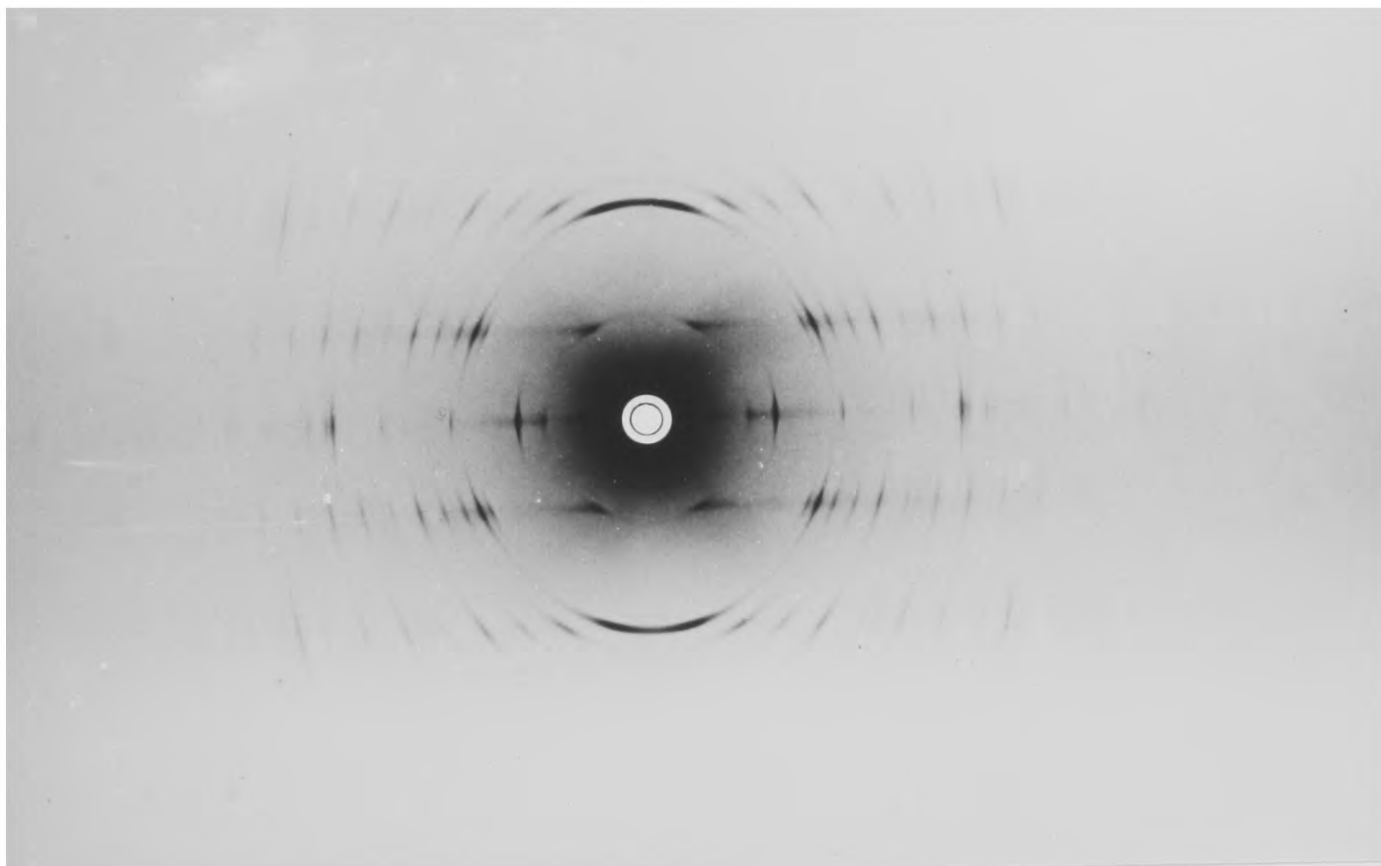


Figure 2.2. X-ray fibre photograph of Povlen-type ortho-chrysotile (specimen 8/20F). Taken with Ni filtered Cu radiation.

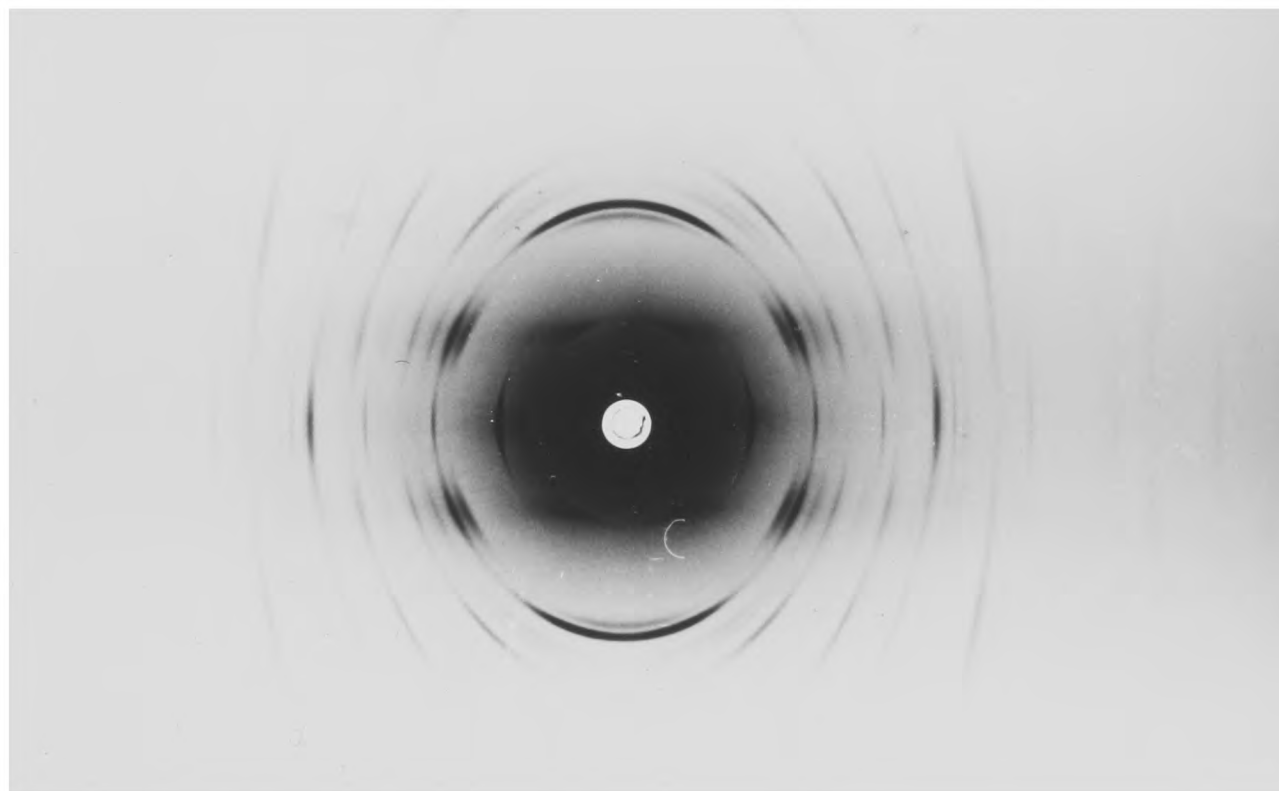


Figure 2.3. X-ray fibre photograph of Povlen-type clino-chrysotile (specimen 9652). Taken with Ni filtered Cu radiation.

An example of the fibre photographs of Povlen-type clino-chrysotile which have been examined, is given in figure 2.3. On some of these photographs weak 201 type reflections, due to minor amounts of ortho-chrysotile, were detected. Other second layer reflections can be indexed as 201 and $20\bar{1}$ reflections from a two-layer clino-chrysotile, and it was at first thought that these reflections were linked along Debye arcs to the extra reflections on the first layer line, much as in Povlen-type ortho-chrysotile (figure 2.2). This relationship between first and second layer line reflections led to the interpretation of Povlen-type chrysotile in terms of the helical model, to be described in section 2.3.2.

Dispersed fibre samples from the ortho-chrysotile specimen which gave the x-ray fibre pattern of figure 2.2 were examined by electron microscopy.* Specimens were dispersed ultrasonically in distilled water and transferred with a dropper on to 3.05mm Cu grids, with or without a thin carbon supporting film. Electron micrographs (figure 2.6) resemble those of normal, silky chrysotiles except that the fibril diameters tend to be greater than is usual - greater than $700\text{ \AA}$ compared with an average outer diameter of below $\sim 500\text{ \AA}$ (Whittaker and Zussman, 1971).

Diffraction patterns given by fibre bundles and, when possible, single fibrils were observed. Some fibres gave diffraction patterns indicating normal ortho-chrysotile, while one gave a pattern in which the diffuse $hk0$ reflections are clearly split into pairs lying above and below the layer lines (see figure 2.7). This phenomenon can be attributed to diffraction from a fibril with a helical cylindrical structure; diffraction phenomena arising from fibrils based on a helical cylindrical lattice are discussed in section 2.3.2.3.

The majority of fibres observed, however, gave diffraction patterns similar to those from normal ortho-chrysotile, but which showed extra reflections on the first layer line, in the region of the tail of 130. As is shown in

* An A.E.I. E.M.6.G. was used for all electron microscopy.

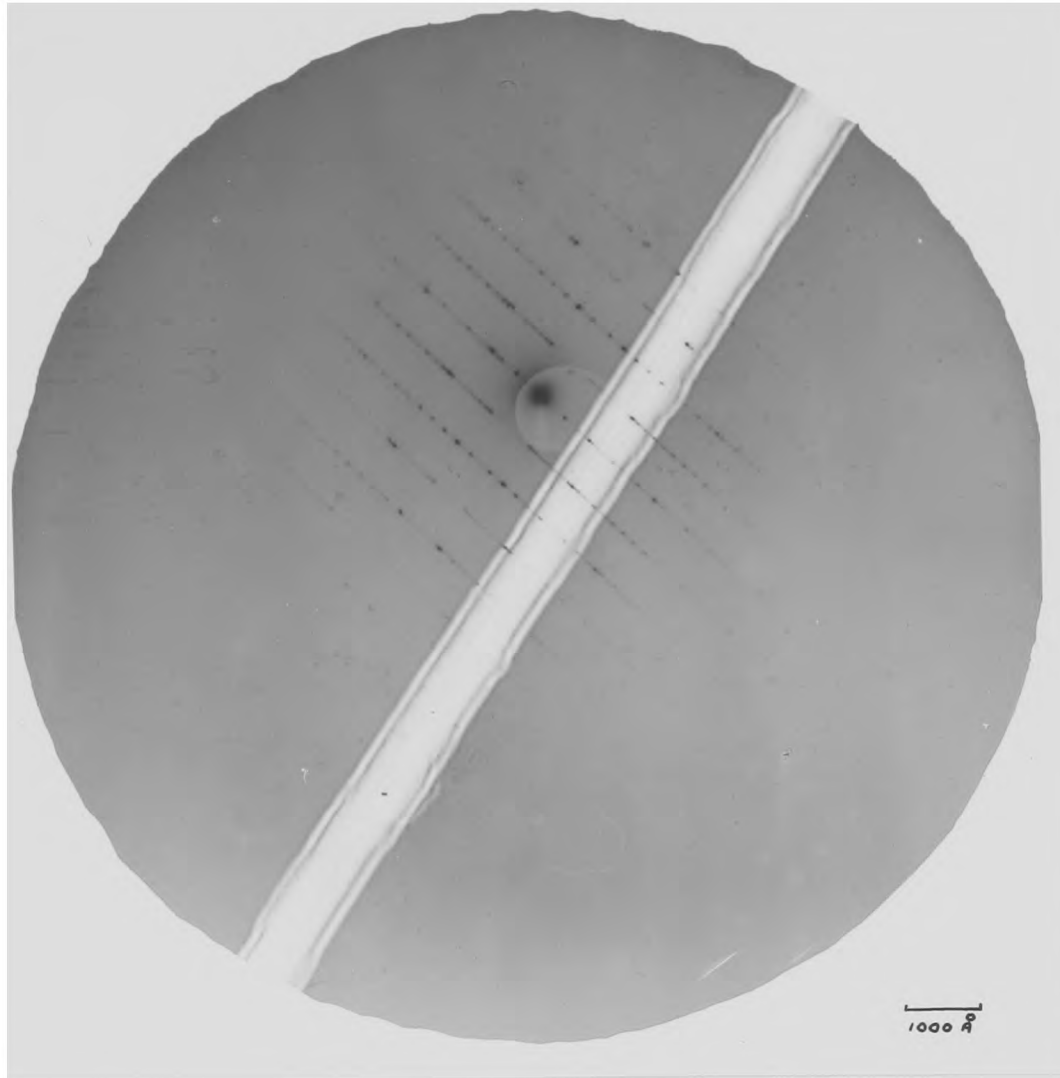


Figure 2.4. Electron micrograph of an isolated fibre of Povlen-type ortho-chrysotile and its diffraction pattern (specimen 8/20F).

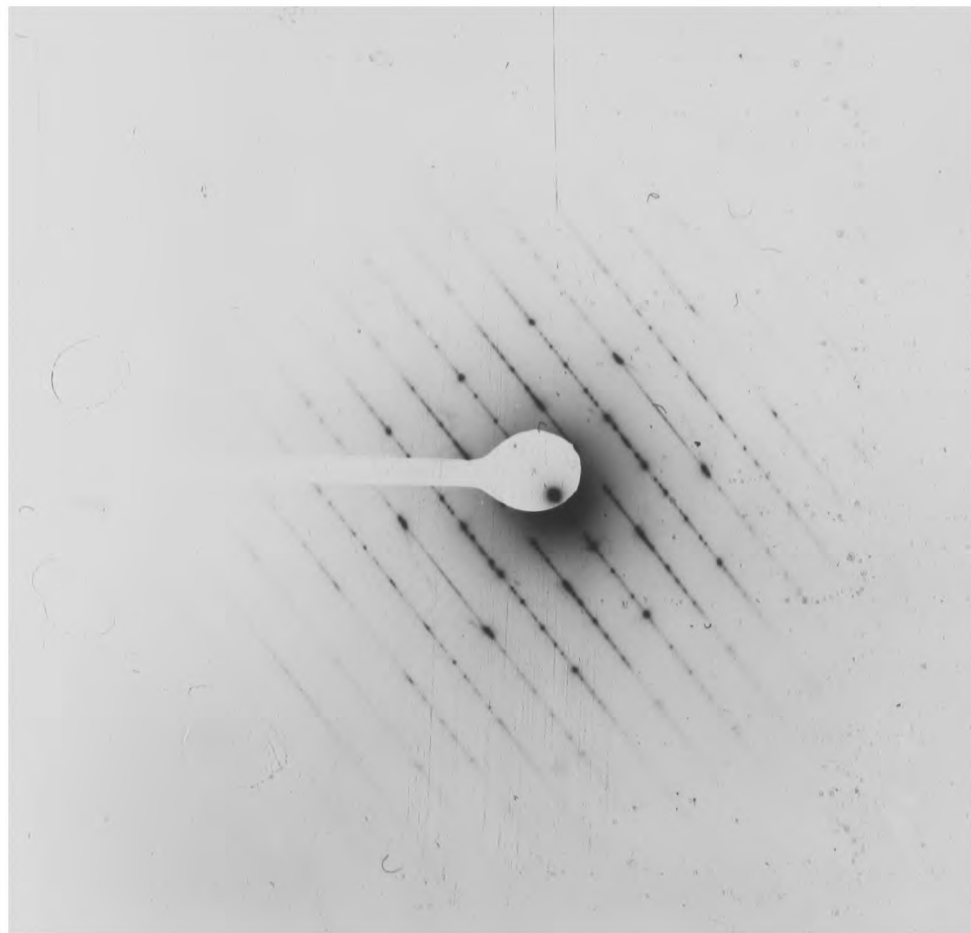
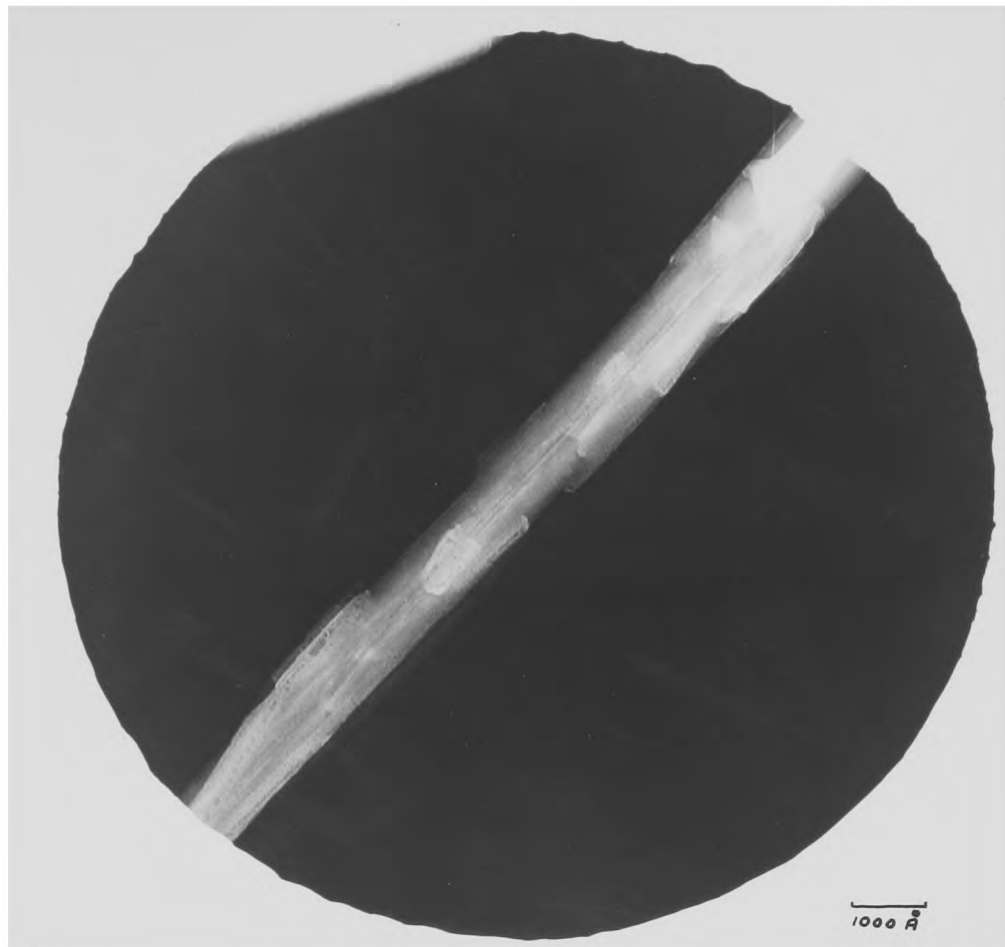


Figure 2.5. Electron micrograph of Povlen-type clino-chrysotile fibre and its diffraction pattern (specimen 9652).

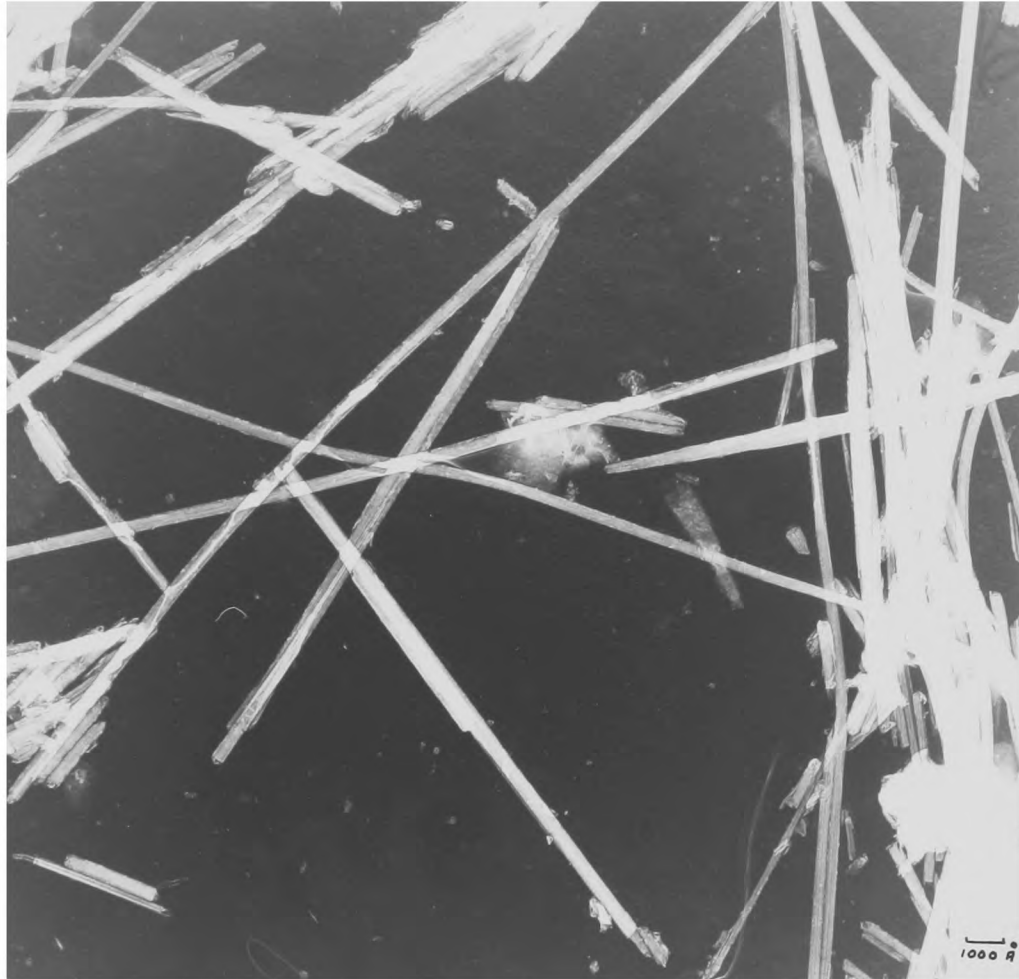


Figure 2.6. low magnification electron micrograph of dispersed fibres of specimen 8/20F.

figure 2.4¹³ (or by measurement) these extra spots on the first layer line lie at the same θ angles as the reflections indexed as 201 type.

Dispersed fibre samples from the Povlen-type clino-chrysotiles from Zermatt (Nos. 3950, 3953, 9652) were also examined in the electron microscope. Examples of the diffraction patterns and micrographs obtained are reproduced in figure 2.5. Once again, a noticeable feature of the diffraction patterns is the presence on the first layer line of sharp reflections, lying to the high angle side of the 130 reflection. The fibres are seen in the micrographs to be somewhat coarser than is usual for chrysotile.

Thus, the electron diffraction patterns from Povlen-type chrysotiles display similar features to the x-ray fibre photographs, but without the powder rings which can be attributed to the effects of misorientation of fibrils, within a fibre bundle. In the light of the observations of morphology in the electron microscope it is necessary to interpret the diffraction effects in terms of a model which permits a single unit (or at most a very few units) to give an electron diffraction pattern exhibiting rotational symmetry about the fibre axis.

2.3. Interpretation

In view of the requirement for a model possessing rotational symmetry about the fibre axis an effort was made initially, to interpret the diffraction phenomena of Povlen-type chrysotiles within the context of a cylindrical model, similar to that of normal chrysotile. These investigations are discussed in the following section (2.3.1). This approach was not, however, fruitful and as a next step the feasibility of a model, derived by a variation in the orientation of structural features was investigated (Section 2.3.2). After initially promising results this model too was found to be inadequate and in a third approach, a model based on flat layers was developed. This is the model adopted for Povlen-type chrysotile, and its development is described in section 2.3.3.

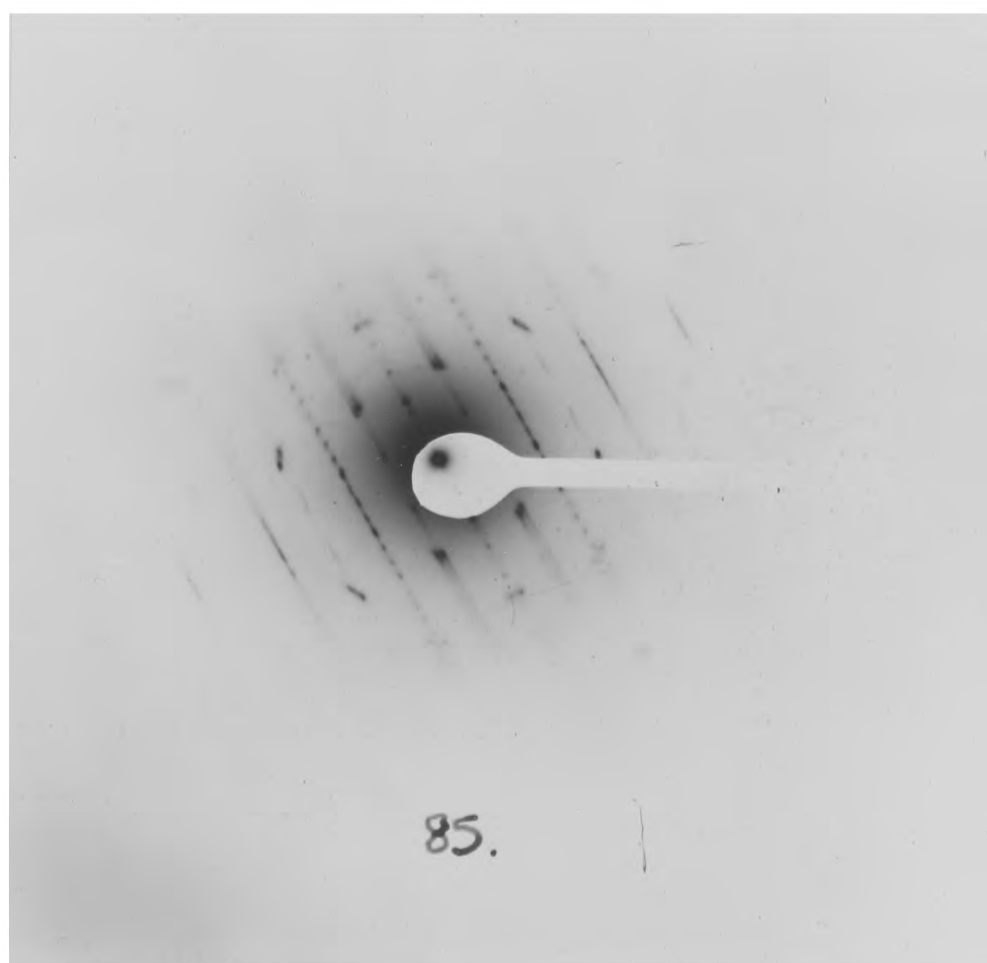
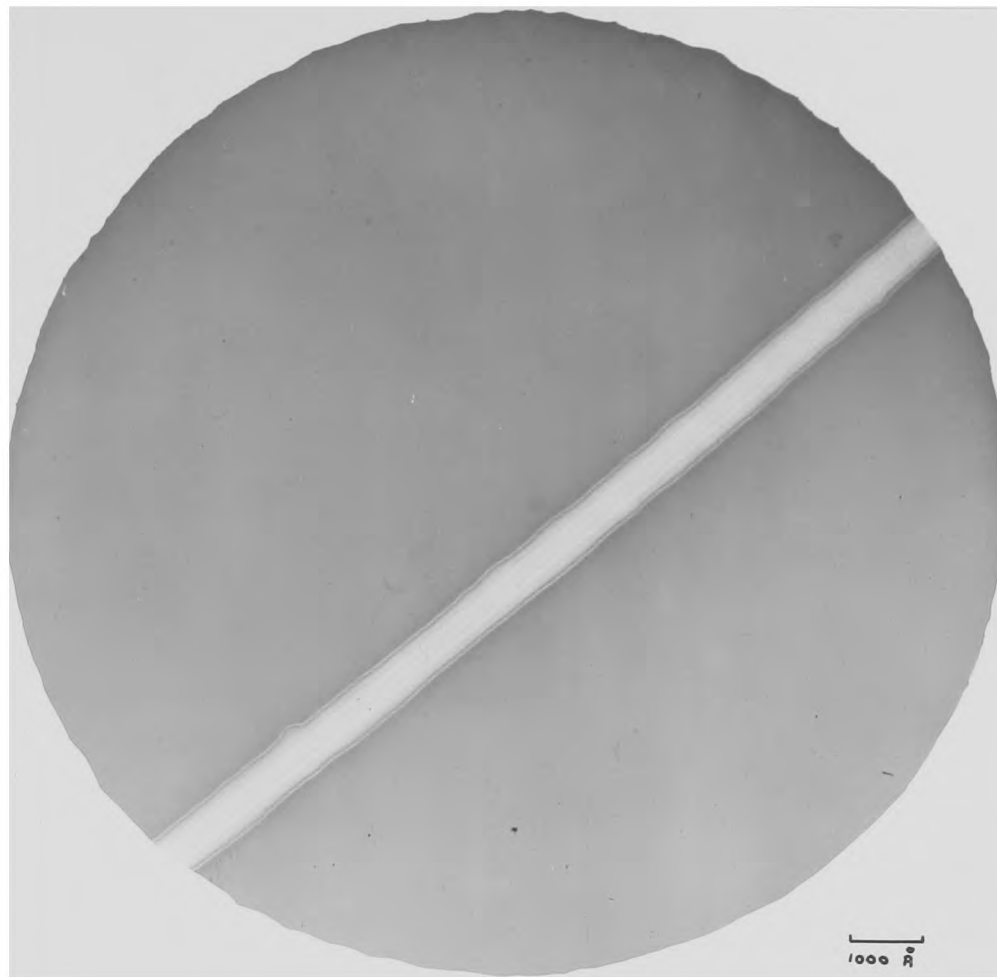


Figure 2.7. Electron micrograph of a fibre from specimen 8/20F and its diffraction pattern, showing splitting of the diffuse reflections.

2.3.1 Variation of fibre parameters

The results of computations of intensity profiles for some of the diffuse reflections of chrysotile will be presented in this section*. The aim of the computations, namely to throw some light on a possible model for Povlen-type chrysotile was not achieved, but the investigation represents an extension of the treatment presented by Whittaker (1957), and is therefore discussed in some detail. The diffraction effects arising from a variation in fibre parameters - in particular the diameters and wall thicknesses of the fibrils making up the fibre bundles - have been considered.

Whittaker (1956c, 1957) derived an expression giving "the intensity scattered by a regular cylindrical structure into diffuse reflections on the l th layer line" -

$$I(\xi, l) = \frac{2Q^2}{R^2} \sum_m \sum_K P_m^2 \left\{ \left| \sum_j f_j \exp \left[2\pi i l \frac{z_j}{c} \right] J_{K P_m} \left(P_m \frac{b_{m,j}}{b} \cdot k \right) \cos 2\pi \frac{K y_j}{b} \right|^2 + \left| \sum_j f_j \exp \left[2\pi i l \frac{z_j}{c} \right] J_{K P_m} \left(P_m \frac{b_{m,j}}{b} \cdot k \right) \sin 2\pi \frac{K y_j}{b} \right|^2 \right\}$$

Equation 2.1

(Whittaker, (1957), equation (1), p.149).

The summations extend over the atoms (j) in the structural unit of each of the layers (m) in the structure and over integral values of K (the order of reflection). The meanings of the symbols used were given by Whittaker as follows -

" Q is the x-ray scattering function for an electron,

R is the distance of the point of observation from the specimen,

P_m is the number of repeating units in the circumference of the m th layer.

f_j is the scattering factor of the j th atom,

* In order to facilitate comparison with Whittaker's treatment the axial convention used by that author is here maintained, i.e. the c -axis is the fibre axis and the diffuse reflections have indices of the type $0kl$. The discussion is restricted to a consideration of reflections on the first layer line since it is primarily in this region of the fibre photographs that the unusual features of Povlen-type chrysotile have been observed.

- x_j, z_j are the radial and axial cylindrical co-ordinates of the atom referred to an arbitrary origin in the neutral surface of the layer with respect to bending,
- $y_{m,j}$ is the arcual distance of the j th atom in the m th layer from an initial radial plane,
- $b_{m,j}$ is the value of $y_{m,j}$ after which the structure repeats (at the radial co-ordinate x_j in the m th layer),
- b is the value of $b_{m,j}$ on the neutral surface of the layer with respect to bending,
- y_j is defined by the relation $\frac{y_j}{b} = \frac{y_{m,j}}{b_{m,j}}$
- k is the index of reflection in reciprocal space regarded as a continuous variable, i.e. $k = \frac{2\pi}{\lambda} b$."

(Whittaker (1957), p. 149).

The origin of m is taken to be at the axis of the cylindrical fibril, so that layer m has a radius of ma ($a = 7.3 \text{ \AA}$). Summations were extended over the layers $m = 3$ to $m = 40$. The lower limit to m was adopted as representing an apparently reasonable (though arbitrary) minimum internal radius for chrysotile fibrils, while the upper limit, $m = 40$ was imposed by the need to avoid the use of excessive computer time, which would otherwise be required for the evaluation of Bessel functions of very high orders.

Whittaker (1957) showed that when the effects of equivalent positions in the two dimensional space group appropriate to the cylindrical projection of the chrysotile layer onto (100) are considered, terms involving $\sin(2\pi Ky_j/b)$ in expression 2.1 vanish. He went on to show that equation 2.1 could then be expressed, for a given value of K , in a form convenient for computation, given below -

$$I(\xi, l) = \frac{8Q^2}{R^2} \sum_m p_m^2 \left| \sum_j u_j f_j \exp \left[2\pi i l \frac{z_j}{c} \right] \cos 2\pi \frac{Ky_j}{b} J_{Kp_m} \left(p_m \frac{b_{m,j}}{b} k \right) \right|^2$$

(Equation 2.2)

(Whittaker (1957), equation (2), p. 150)

u_j is the multiplicity of the j th atom, appropriate to the particular value of K , as follows -

$$\begin{array}{l} u_{O_1} = 1 \\ u_{Si} = 2 \end{array} \left. \vphantom{\begin{array}{l} u_{O_1} = 1 \\ u_{Si} = 2 \end{array}} \right\} \text{ for all reflections}$$

$$u_{O_2} = 2 \quad \text{for } K = 2n$$

$$u_{O_2} = 0 \quad \text{for } K \neq 2n$$

All other values of u_j are 3 for $K = 3n$

and 0 for $K \neq 3n$

After comparing the observed and calculated profiles of some of the diffuse reflections of chrysotile, Whittaker (1957, p. 151) suggested that in order to suppress the oscillatory component in the tails of the calculated profiles, all the layers in the structure should be "assigned statistical weights falling smoothly to zero as their radii increase or decrease from some mean value."

Whittaker pointed out that such a scheme is also physically reasonable. In a particular fibril only one layer can take on a strain-free radius of curvature; the other layers will all be subject to a degree of strain which increases as their curvature increases or decreases from that of the strain-free layer. These strained layers might be expected to occur less frequently as the strain increases.

The growth model adopted by Whittaker was such that the strain-free layer (the m_0^{th} layer) is presumed to have formed first and subsequent growth, inwards and outwards, occurred by the deposition of layers of lesser and greater radii. The appropriate statistical weight to be applied to the layer is then of the form* -

* Possible weighting schemes were discussed more fully by Whittaker (1956c, p. 147 ff).

$$\left. \begin{array}{l} \prod_{m_0}^m \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} \quad \text{when } m > m_0 \\ \text{or } \prod_m^{m_0} \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} \quad \text{when } m < m_0 \end{array} \right\} \text{Equation 2.3}$$

t is an undetermined constant

(Whittaker (1957), equation (3) p.152)

Whittaker went on to derive expressions for the distribution of fibril sizes associated with particular values of m_0 and t -

$$\left. \begin{array}{l} {}_oP_m = \prod_{m_0}^m \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} - \prod_{m_0}^{m+1} \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} \\ {}_IP_m = \prod_m^{m_0} \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} - \prod_{m-1}^{m_0} \exp \left\{ -tm \left(\frac{1}{m} - \frac{1}{m_0} \right)^2 \right\} \end{array} \right\} \text{Equation 2.4}$$

(Whittaker (1957), page 153)

${}_oP_m$ and ${}_IP_m$ are the frequencies of fibrils having the m^{th} layer as the outermost and innermost layer, respectively.

It was thought that the unusual diffraction effects from Povlen-type chrysotile might be due to an abundance of (perhaps thin-walled) fibrils of abnormally large diameter, which had been suggested by observation in the electron microscope of somewhat coarser fibrils than usual. A computer program, 'WATES'* was written in order to investigate the fibril diameter and wall thickness distributions implied by particular values of m_0 and t, and to calculate appropriate statistical weights.

Whittaker (1957) initially adopted values of $m_0 = 9$, $t = 10$ in the calculation of the profiles of diffuse reflections. However, from consideration of the sharpness of Okl reflections on their low-angle side and from the displacement of their maxima (from integral values of b^*)** he concluded that values of $m_0 = 12$ and $t = 20$ would be more appropriate to the

* See Appendix A.

** consideration of these features allows an estimate of fibril diameter to be made.

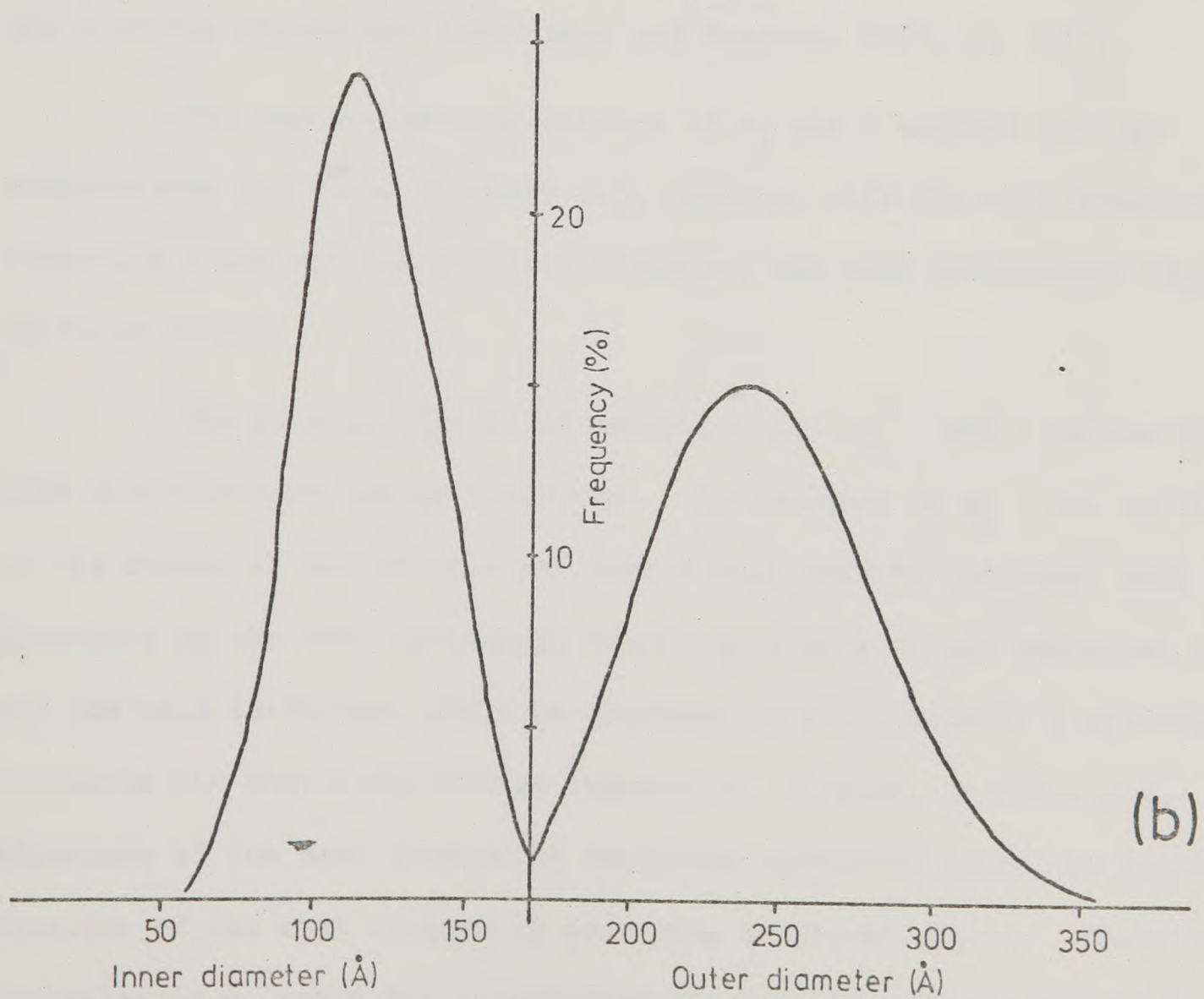
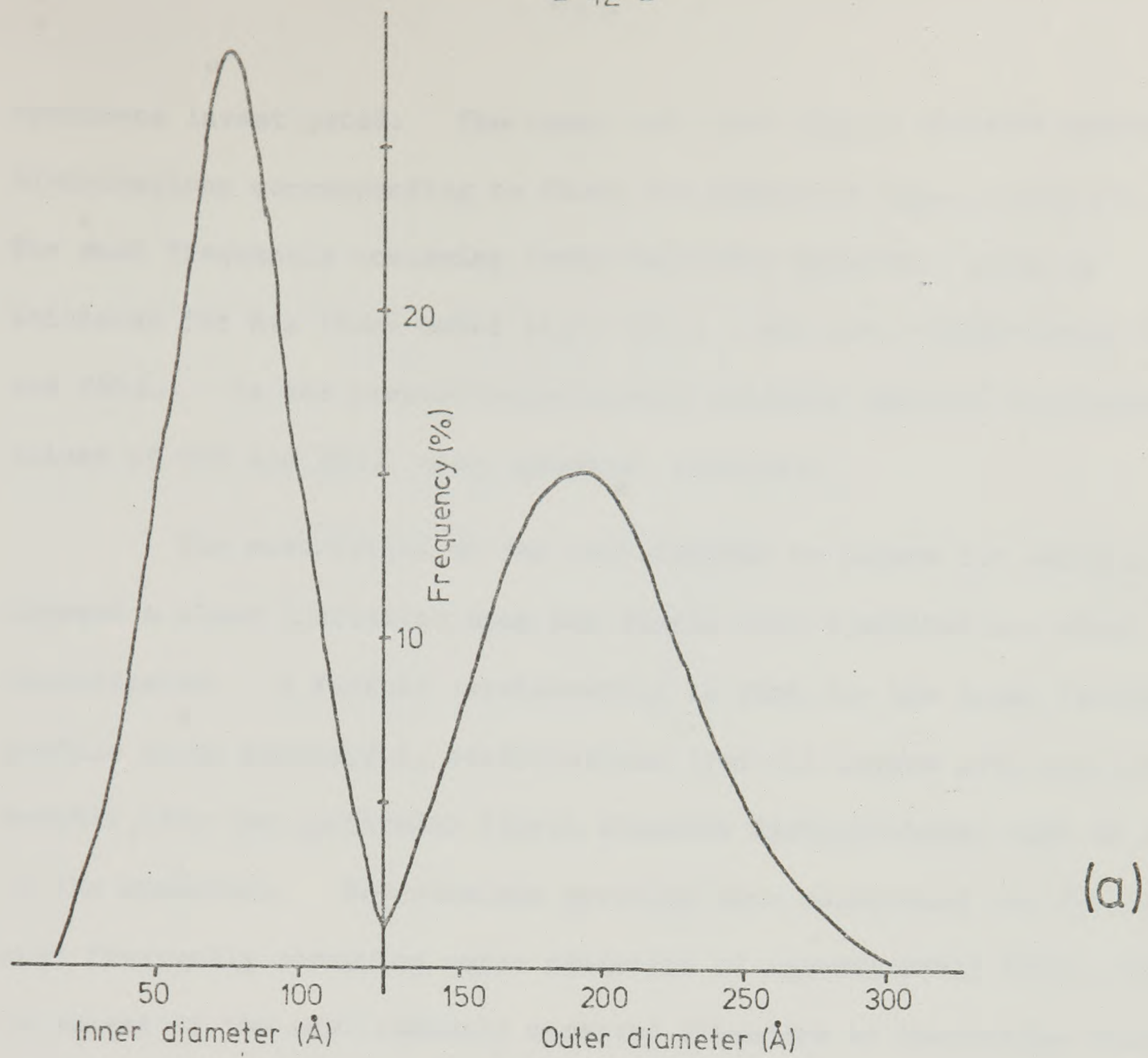


Figure 2.8. Frequencies distributions of the inside and outside diameters of fibrils appropriate to (a) $m_0 = 9$, $t = 10$ and (b) $m_0 = 12$, $t = 20$. See text for discussion.

specimens investigated. The inner and outer fibril diameter frequency distributions corresponding to these two cases are shown in figure 2.8. The most frequently occurring inner and outer diameters given by Whittaker for his final model ($m_0 = 12$, $t = 20$) were respectively 110 and 260 Å. In the present calculations slightly smaller, corresponding values of 100 and 250 Å were, however, obtained.

The restriction of the calculations to layers for which $m \leq 40$ imposed a clear limitation upon the fibril size distributions which could be investigated. A further consideration is that for the final (weighted) profile to be meaningful, contributions from all layers with appreciable weights (for the particular fibril diameter distributions) must be included in the summation. Nevertheless profiles were calculated for fibres with most frequently occurring outer diameters of approximately 450 Å, considerably in excess of the most commonly observed diameters of chrysotile fibrils in the electron microscope (Whittaker and Zussman, 1971, p. 161).

The particular combinations of m_0 and t adopted for the calculations are given in Table 2.3, together with the most frequently occurring inner and outer fibril diameters and wall thicknesses implied by these values.

The general effects of variation in m_0 and t on the fibril size distributions can be predicted. An increase in m_0 (i.e. an increase in the radius of the strain-free layer) will tend to increase, both the diameters of the most frequently occurring innermost and outermost layers and the wall thickness, while an increase in the constant, t effectively increases the contribution from thin-walled fibrils, by diminishing the diameters of the most frequently occurring outermost layer and increasing the diameter of the most frequently occurring innermost layer. These effects of variation in m_0 and t are illustrated diagrammatically in figure 2.9.

TABLE 2.3

Values of the constants m_0 and t adopted in the calculation of statistical weights, and the inner and outer diameters and wall thickness of the fibrils which most frequently occur with these values

m_0	t	size parameters of most frequently occurring fibrils		
		inner diam.	outer diam.	wall thickness
		(Å)	(Å)	(No. of layers)
9	1	29.3	321.9	20
12	2	29.3	365.8	23
12	3	29.3	336.5	21
12	5	58.5	307.2	17
12	10	87.8	278.0	13
15	5	73.2	380.4	21
15	10	102.4	351.1	17
15	20	131.7	321.9	13
20	20	160.9	424.3	18
20	40	190.2	395.0	14
20	100	219.5	365.8	10
20	250	234.1	336.5	7
20	500	248.7	321.9	5
20	1000	263.3	321.9	4
25	80	263.3	468.2	14
25	100	278.0	453.5	12
25	250	292.6	424.3	9
25	500	307.2	409.6	7
25	1000	321.9	395.0	5

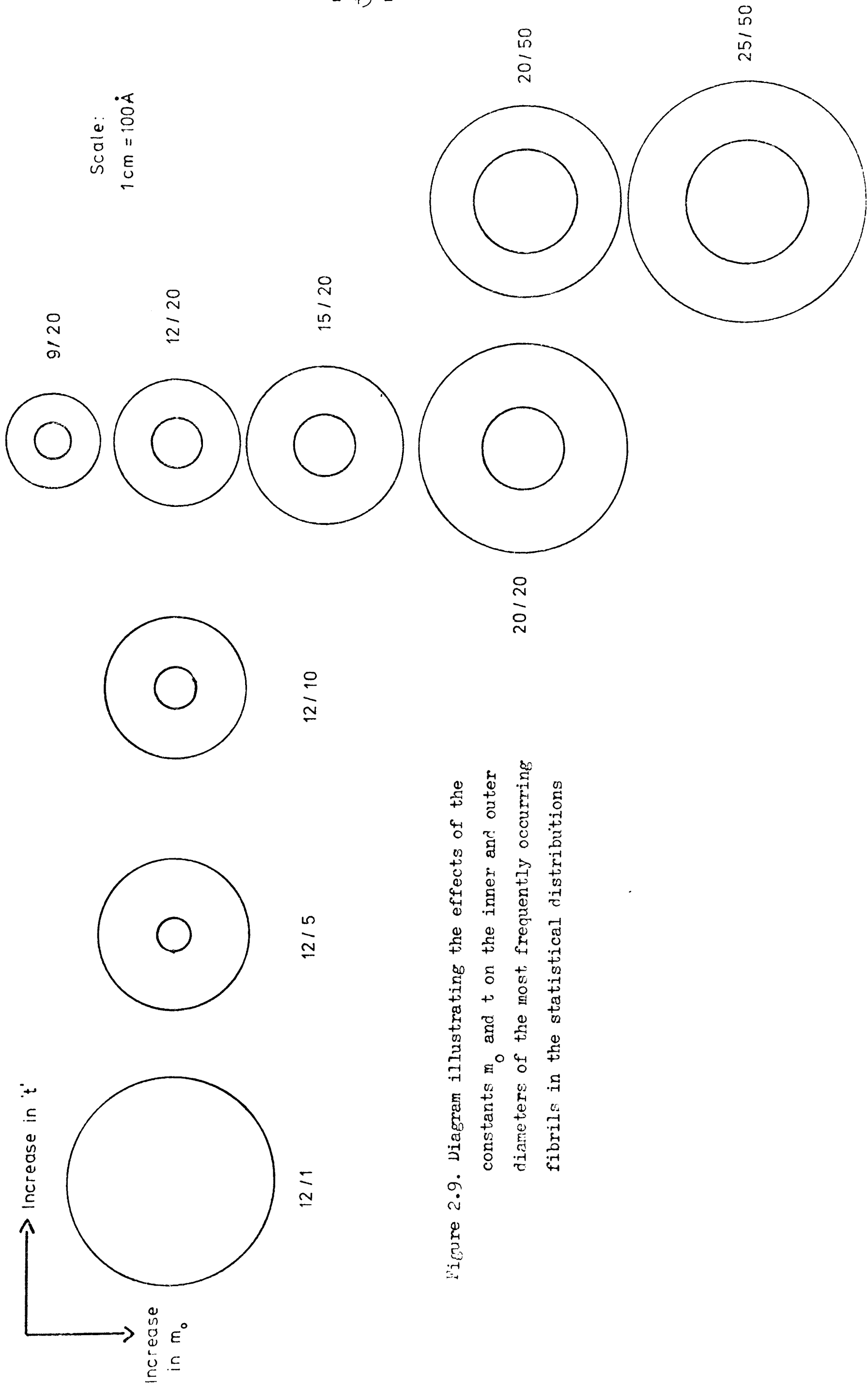


Figure 2.9. Diagram illustrating the effects of the constants m_o and t on the inner and outer diameters of the most frequently occurring fibrils in the statistical distributions

Intensity contributions from layers, $m = 3$ to 40 were calculated from expression 2.2 using a computer program, 'ORTHO': The atomic co-ordinates given by Whittaker (1957, Table 1) were used in the calculations; they are reproduced in Table 2.4. For the sake of simplicity and direct comparability with the earlier work, the scattering factors used were the empirical temperature corrected values of Bragg and West (1928, Table VII). The facility to apply the weighting scheme discussed above was incorporated into the program. In this way appropriately weighted profiles were computed for some of the diffuse reflections of chrysotile, based on a regular cylindrical lattice (orthorhombic or monoclinic of the first kind, Table 1.1).

The results of these computations are most conveniently presented in diagrammatic form and this is done in figure 2.10. A notable feature is the development in some instances, of several sharp maxima following the initial maximum. A further effect is the occurrence of a small maximum at $k \approx K + 1$ in some of the profiles. These effects may to some extent account for the variability ("lumpiness") of the profiles of the diffuse reflections of chrysotile. However, what is considered to be a more satisfactory explanation of this phenomenon, is given in section 2.4. The effects of alteration of fibre parameters on the calculated profiles of the diffuse reflections, particularly 031, do not, however, correspond well with the unusual features observed on fibre diffraction patterns of Povlen-type chrysotile, (figure 2.12).

The possibility was next considered that Povlen-type chrysotile is based upon a helical, cylindrical lattice in which $\alpha + \delta_m = \pi/2$ (see figure 2.16 and section 2.3.2.3 for the meaning of these angles), this being a special case of the anorthic lattice of the second kind (Table 1.1).

* see Appendix A.

TABLE 2.4

Atomic co-ordinates in a single chrysotile layer,
referred to orthogonal axes, with the a-axis*
halved (after Whittaker (1957), Table 1)

	x/a	y/b	z/c
O_1	- 0.326	0	0.025
O_2	- 0.300	0.250	0.273
Si	- 0.234	0.167	0.024
O_3	0	0.167	0.023
OH_1	0	0.500	0.023
Mg_1	0.154	0.500	0.361
Mg_2	0.154	0.167	0.361
OH_2	0.284	0	0.196
OH_3	0.284	0.333	0.196

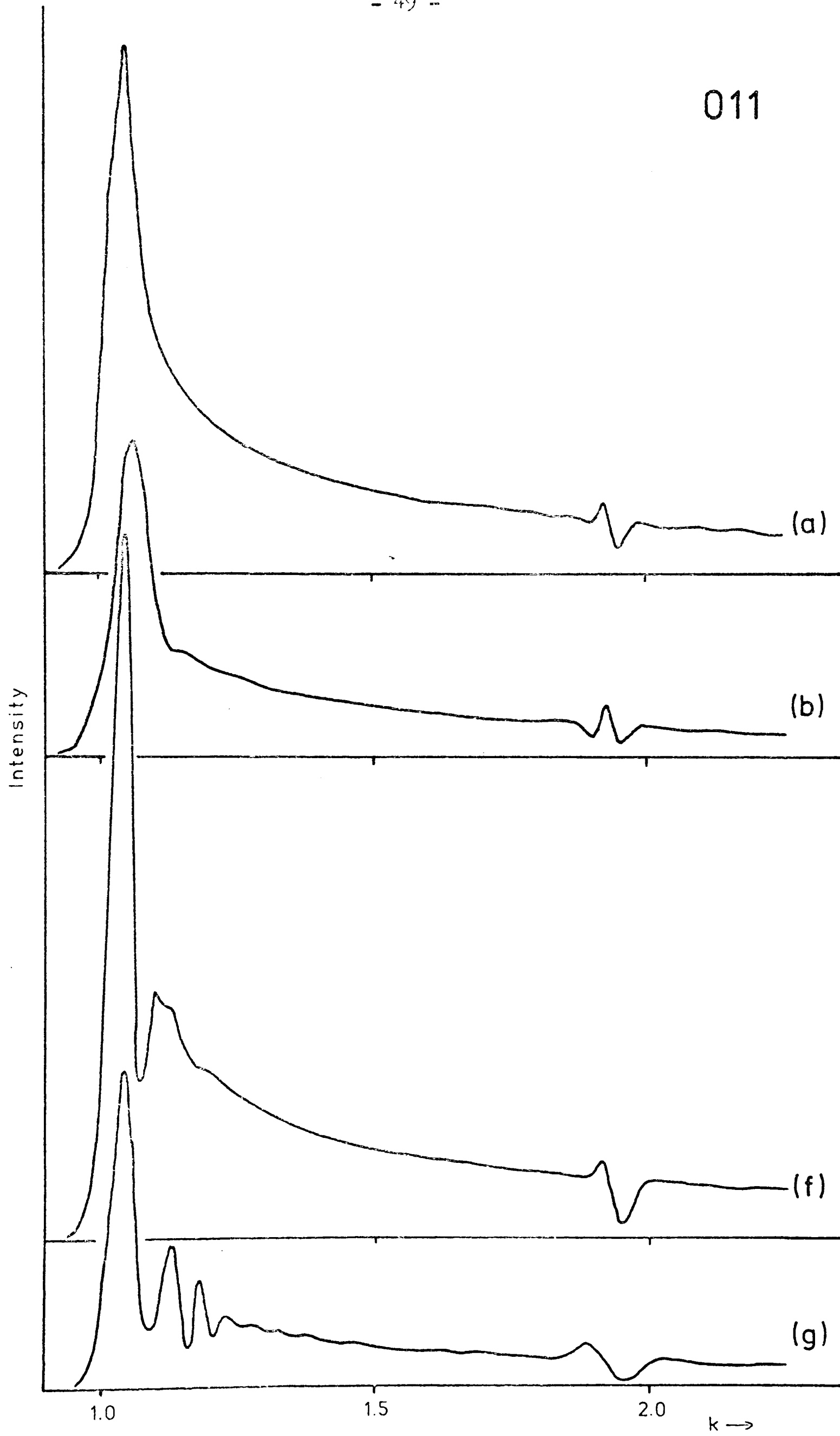
* Where a is approximately 14.6 Å

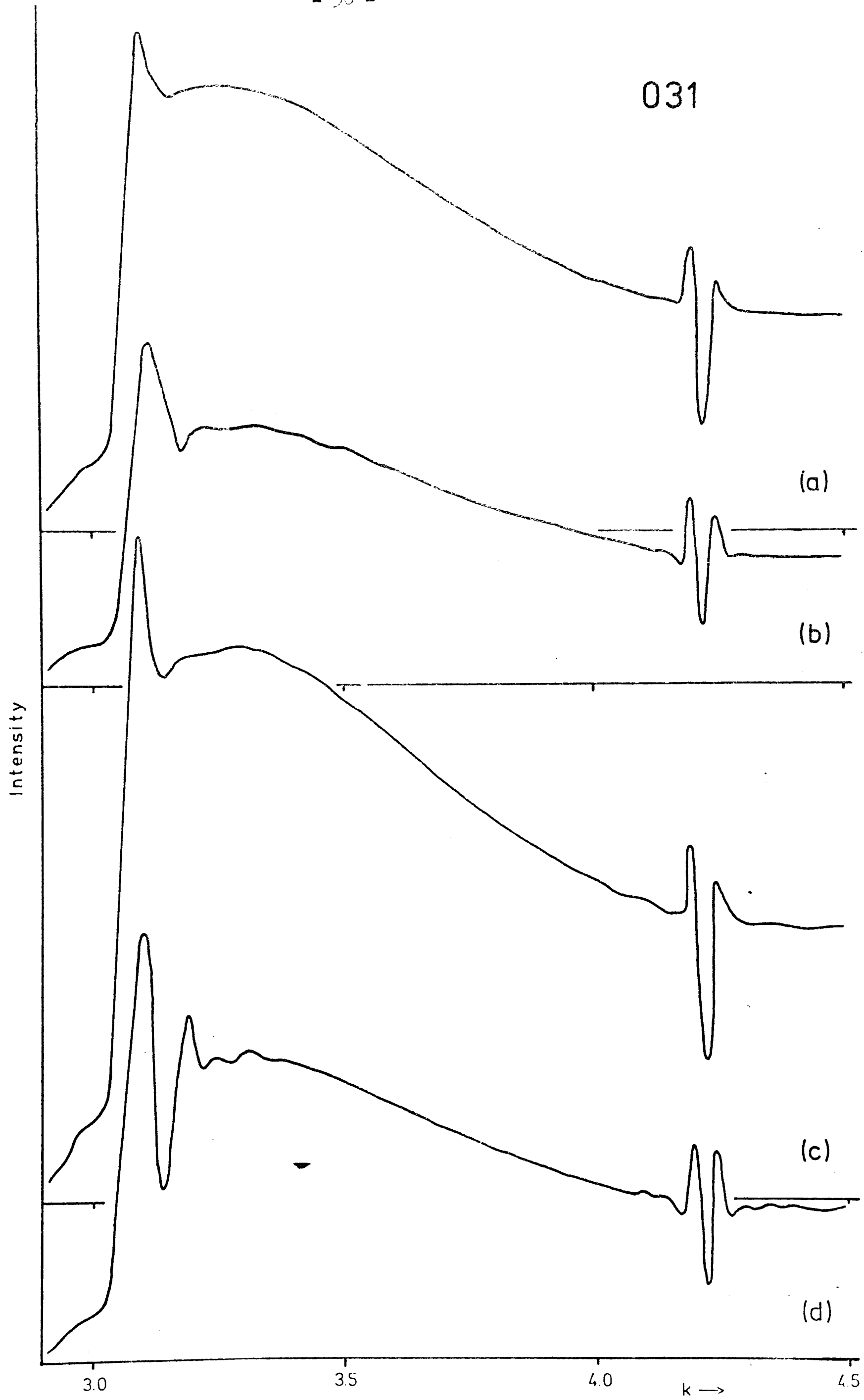
Figure 2.10

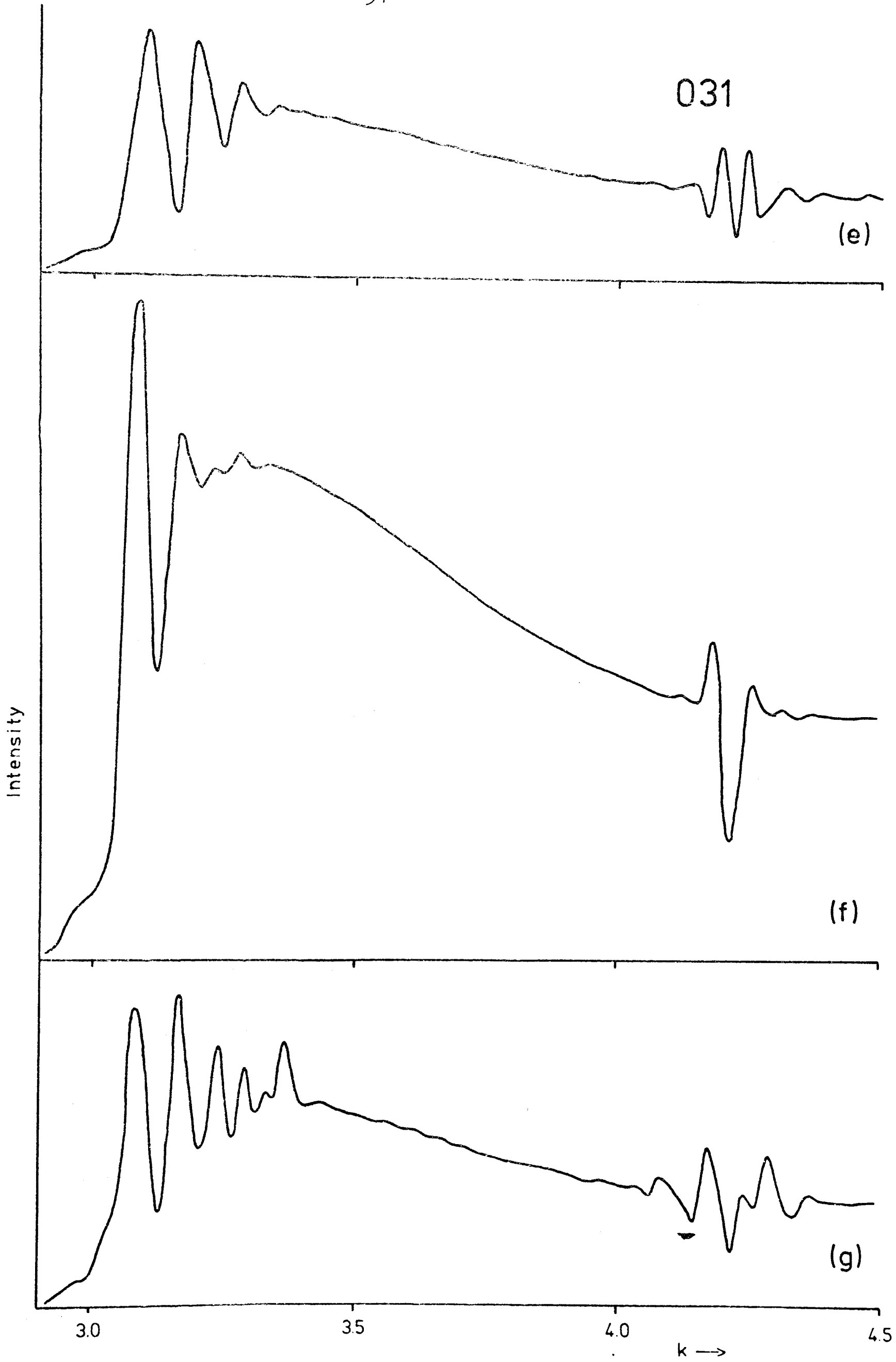
Representative weighted profiles calculated for the 011,031 and 051 reflections of chrysotile. The values of m_o and t adopted in the weighting of each profile are indicated by the following letter code:

- a) $m_o=9$; $t=1$
- b) $m_o=12$; $t=10$
- c) $m_o=15$; $t=5$
- d) $m_o=20$; $t=100$
- e) $m_o=20$; $t=500$
- f) $m_o=25$; $t=100$
- g) $m_o=25$; $t=1000$

011

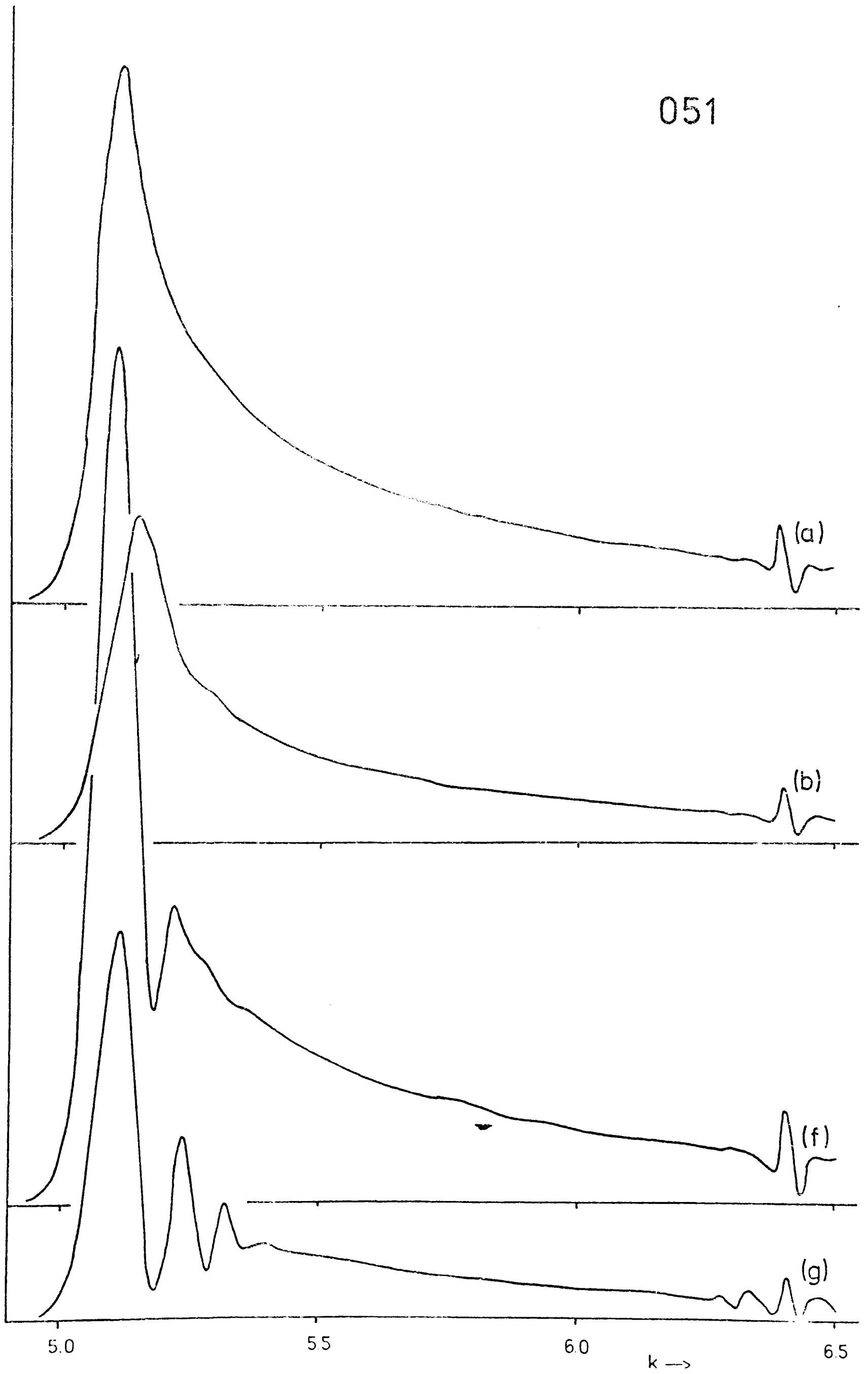






051

Intensity



It was shown by Whittaker (1955a) that if distortions in the cylindrical layers permit the relationship $\alpha + \delta_m = \pi/2$ to be maintained, then the diffuse reflections from such a lattice would not be split to either side of the layer lines.* The intensity of an Ok_l reflection is given by -

$$\frac{Q^2 g^2 b^2}{R^2} \sum_m P_m^2 \left\{ J_{K_{P_m} - N_l}^2(P_m k) + J_{K_{P_m} + N_l}^2(P_m k) \right\}$$

Equation 2.5

(Whittaker (1955a) equation (7), p. 728)

N is the order of the helix.

On the basis of equation 2.5 the profile of the 031 reflection of chrysotile was calculated for $N = 2$, and weighted according to several distributions of fibril diameters. The calculations were carried out using a computer program, 'ORTHOH'**. It is apparent, however, that while fluctuations in intensity occur to the high angle side of the initial maximum (figure 2.11), the computed profiles do not match in detail the observed profiles of the 031 reflection of Povlen-type chrysotile, (figure 2.12).

In the light of these investigations, it seems unlikely that Povlen-type chrysotile can be interpreted in terms of a cylindrical model, which is broadly similar in character to normal chrysotile.

2.3.2 Development of a model based on alternative orientations

2.3.2.1 A possibly analogous effect in magnesite

Unusual diffraction effects, similar to those observed from Povlen-type chrysotile have been noted on fibre photographs of magnesite and of brucite. In these photographs are weak Debye arcs, on each of which are developed spots at positions appropriate to several layer lines.

* The diffuse reflections arising from helical cylindrical lattices are discussed more fully in section 2.3.2.3.

** See Appendix A.



Figure 2.11. Representative weighted profiles calculated for the 031 reflection of helical chrysotile ($N=2$), for the following values of m_0 and t :

- (a) $m_0 = 9, t = 1$
- (b) $m_0 = 25, t = 100$
- (c) $m_0 = 25, t = 1000$

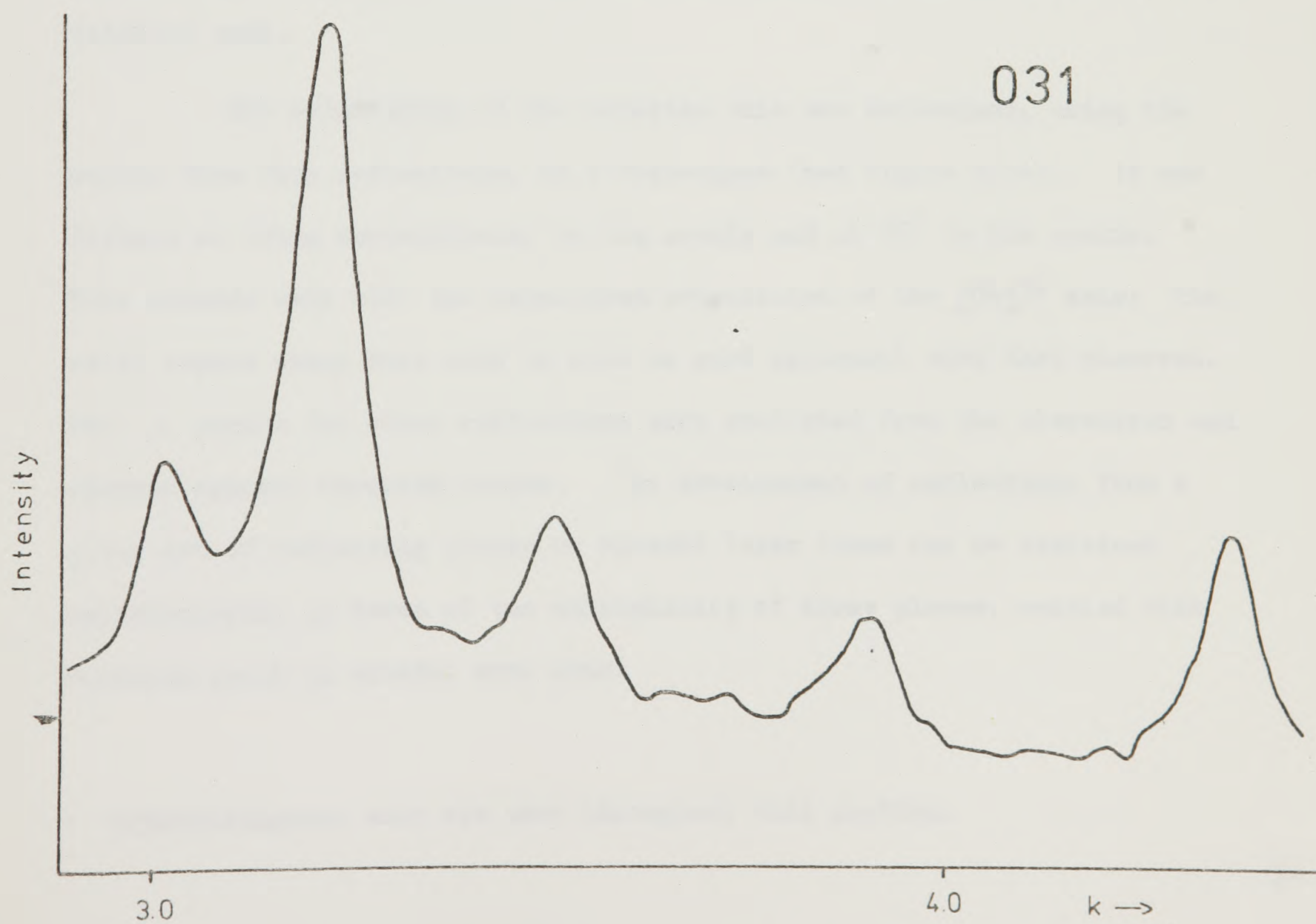
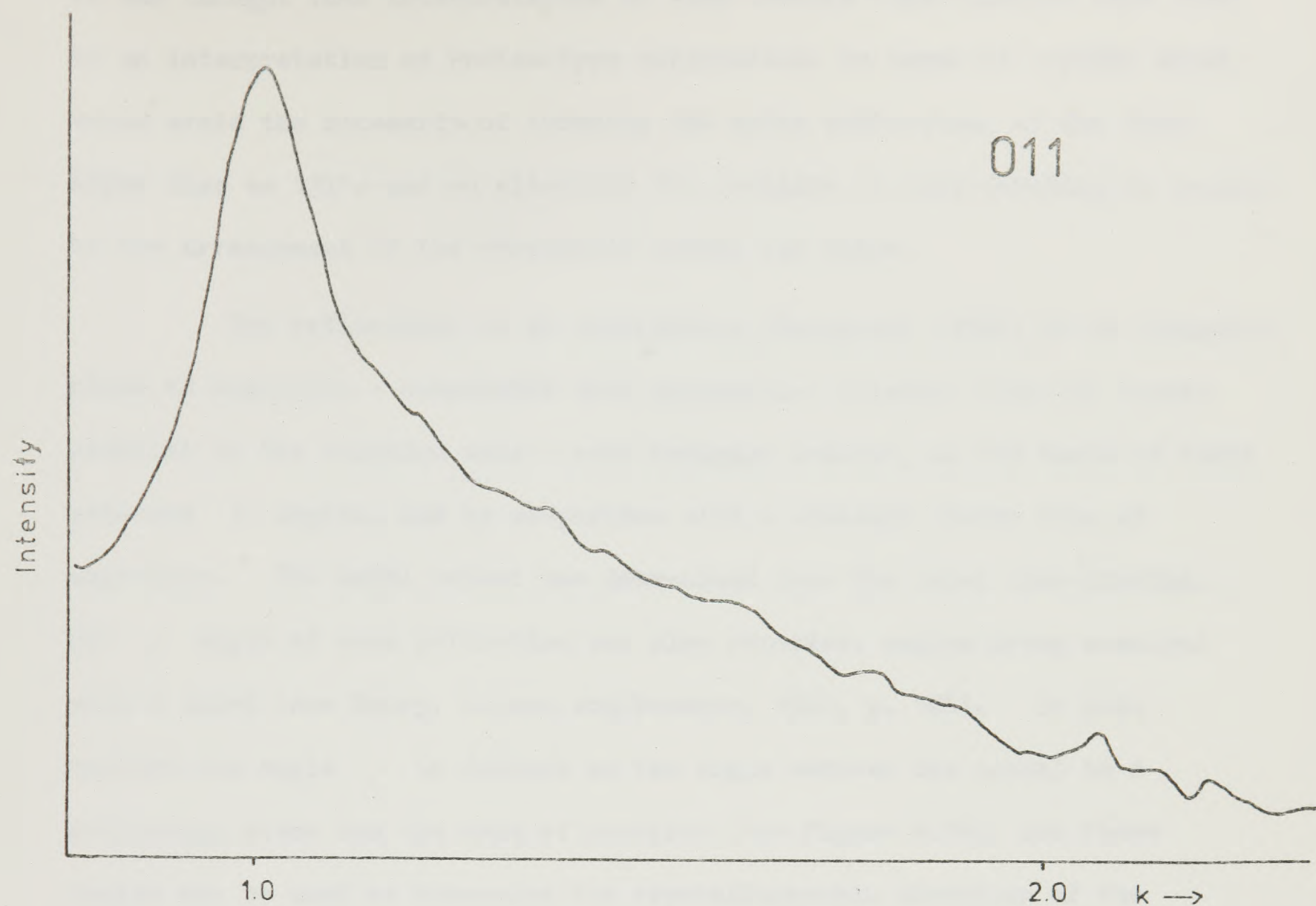


Figure 2.12. Observed profiles of the 011 and 031 reflections of Povlen-type ortho-chrysotile, in x-ray diffraction; specimen 8/20 F.

It was thought that interpretation of this feature might provide some clue to an interpretation of Povlen-type chrysotiles, in terms of a model which would avoid the necessity of indexing the extra reflections of the first layer line as 131's and so alleviate the problems of such indexing in respect of the arrangement of the chrysotile within the fibre.

The reflections on an oscillation photograph (G394) of an elongated plate of magnesite - associated with chrysotile, oriented with the a-axis parallel to the rotation axis - were assigned indices, on the basis of their measured θ angles, and by comparison with a standard powder film of magnesite. The axial repeat was determined from the layer line spacing. The ρ angle of each reflection was also recorded, angles being measured with a chart (see Henry, Lipson and Wooster, 1960, p. 108). In this context the angle ρ is defined as the angle between the normal to a reflecting plane and the axis of rotation (see figure 2.14), and these angles may be used to determine the crystallographic direction of the rotation axis.

The orientation of the rotation axis was determined, using the angles from four reflections, on a stereogram (see figure 2.14). It was defined as lying perpendicular to the a-axis and at 66° to the c-axis. This accords well with the calculated orientation of the $[041]^*$ axis; the axial repeat along this axis is also in good agreement with that observed. The ρ angles for other reflections were predicted from the stereogram and checked against observed values. The development of reflections from a given set of reflecting planes on several layer lines can be explained satisfactorily in terms of the multiplicity of those planes, coupled with rotation about an unusual zone axis.

* Ortho-hexagonal axes are used throughout this section.

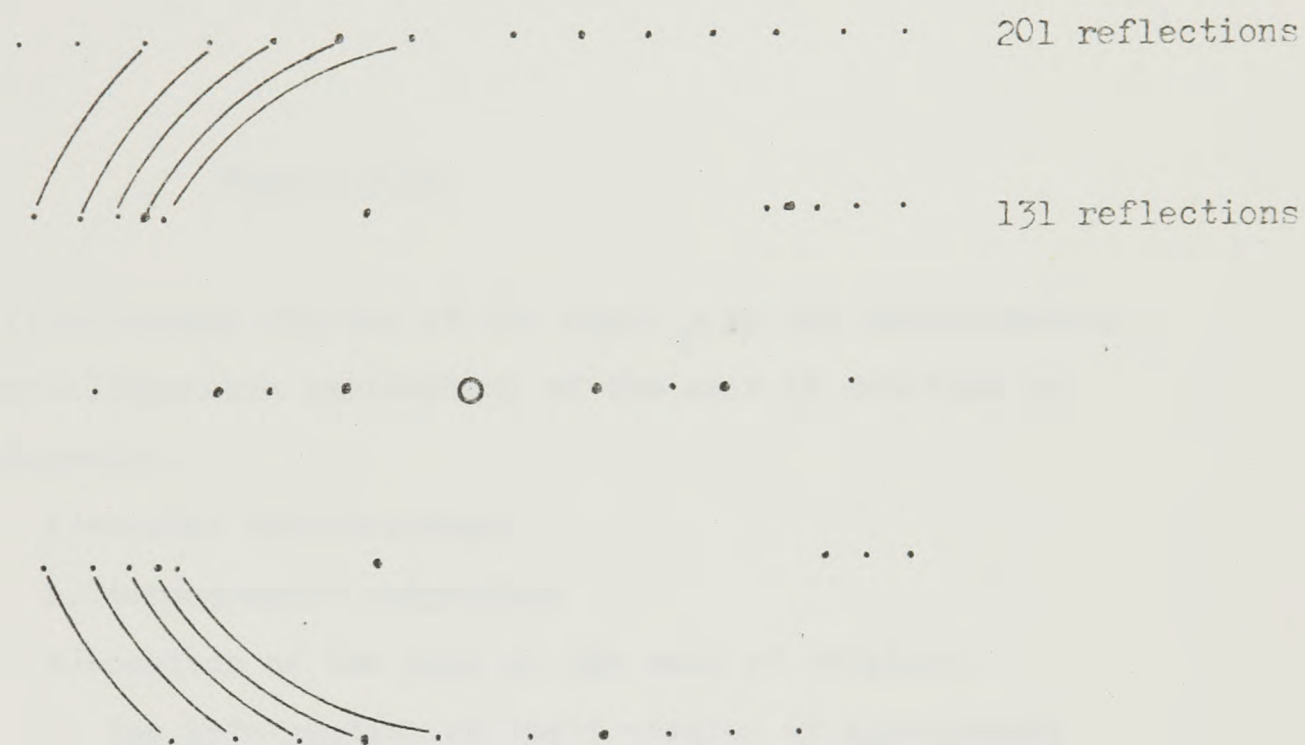


Figure 2.13.

Diagram illustrating the relationship between the 201 and 131 reflections of Povlen-type ortho-chrysotile in electron diffraction.

Figure 2.14

Diagrams illustrating the use of the angle ρ in the determination of the crystallographic orientation of the axis of rotation in x-ray photographs.

a) Angular relationships

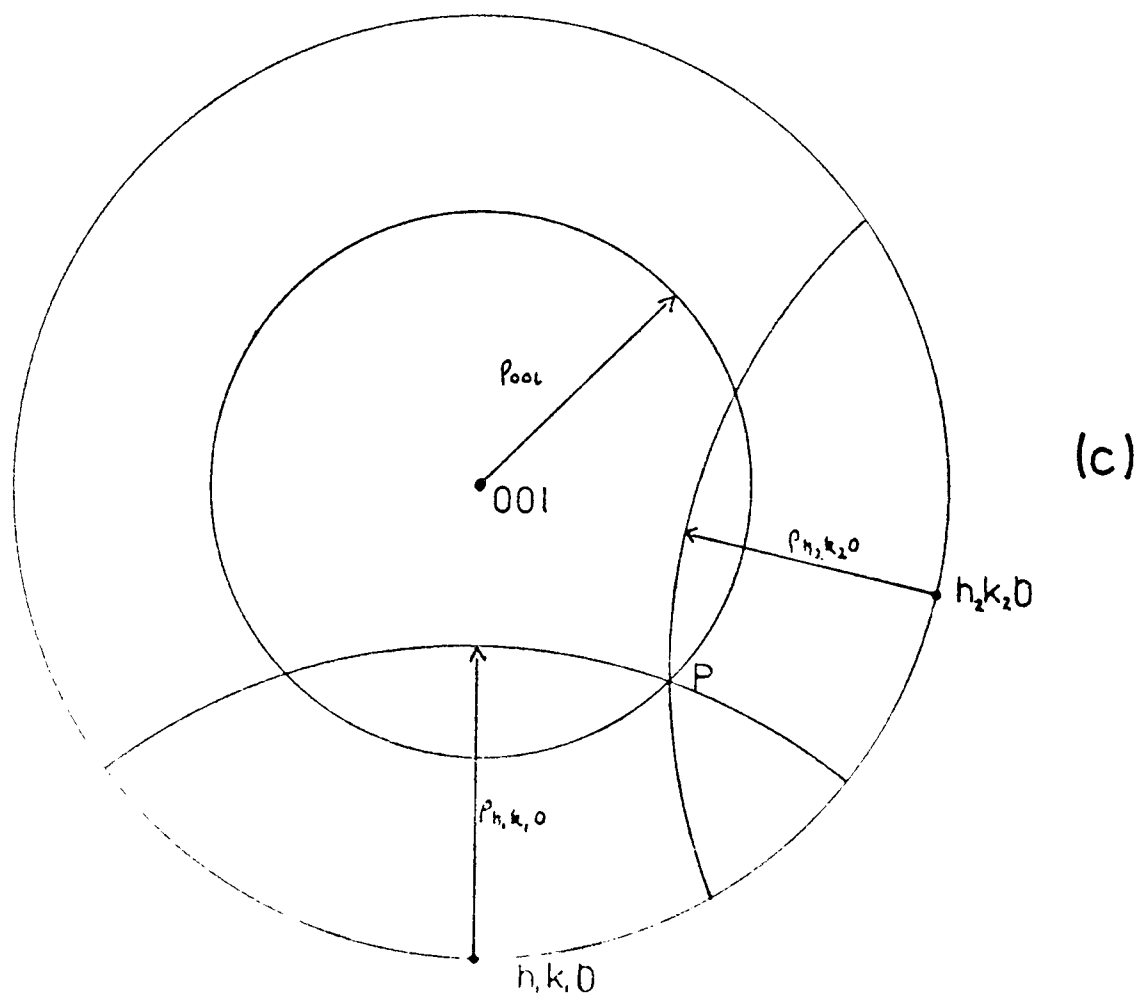
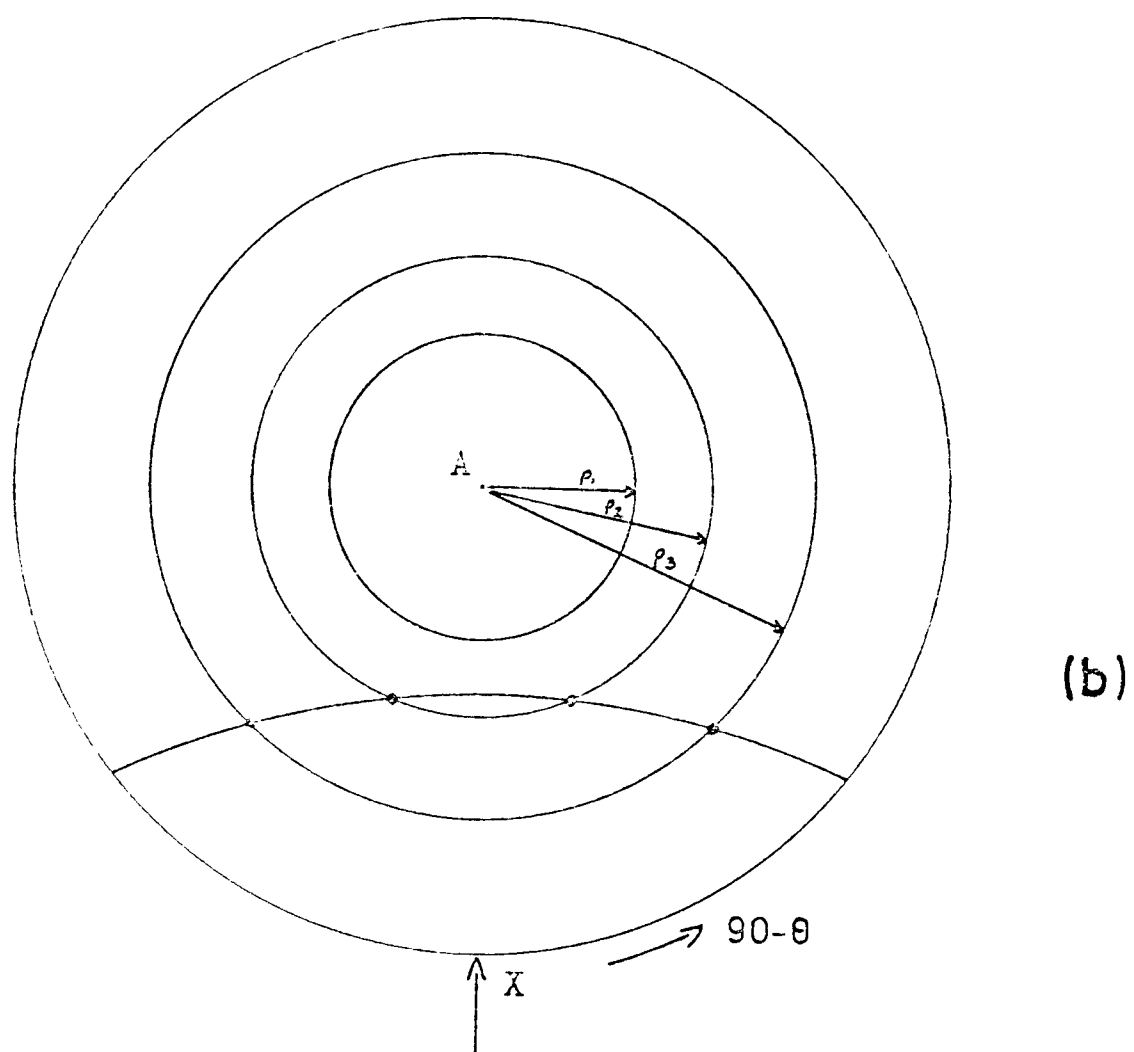
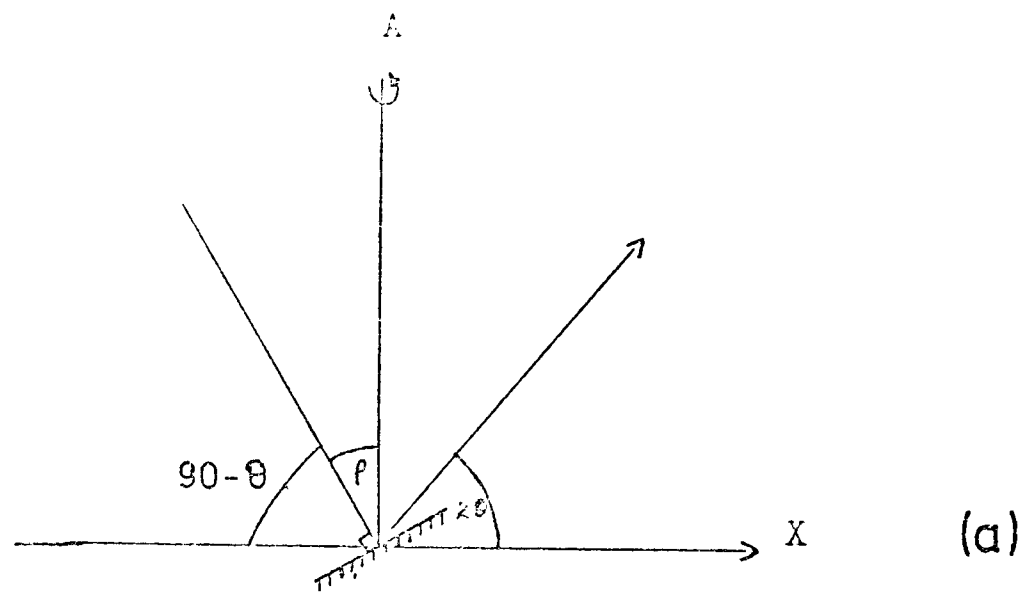
b) Stereographic projection

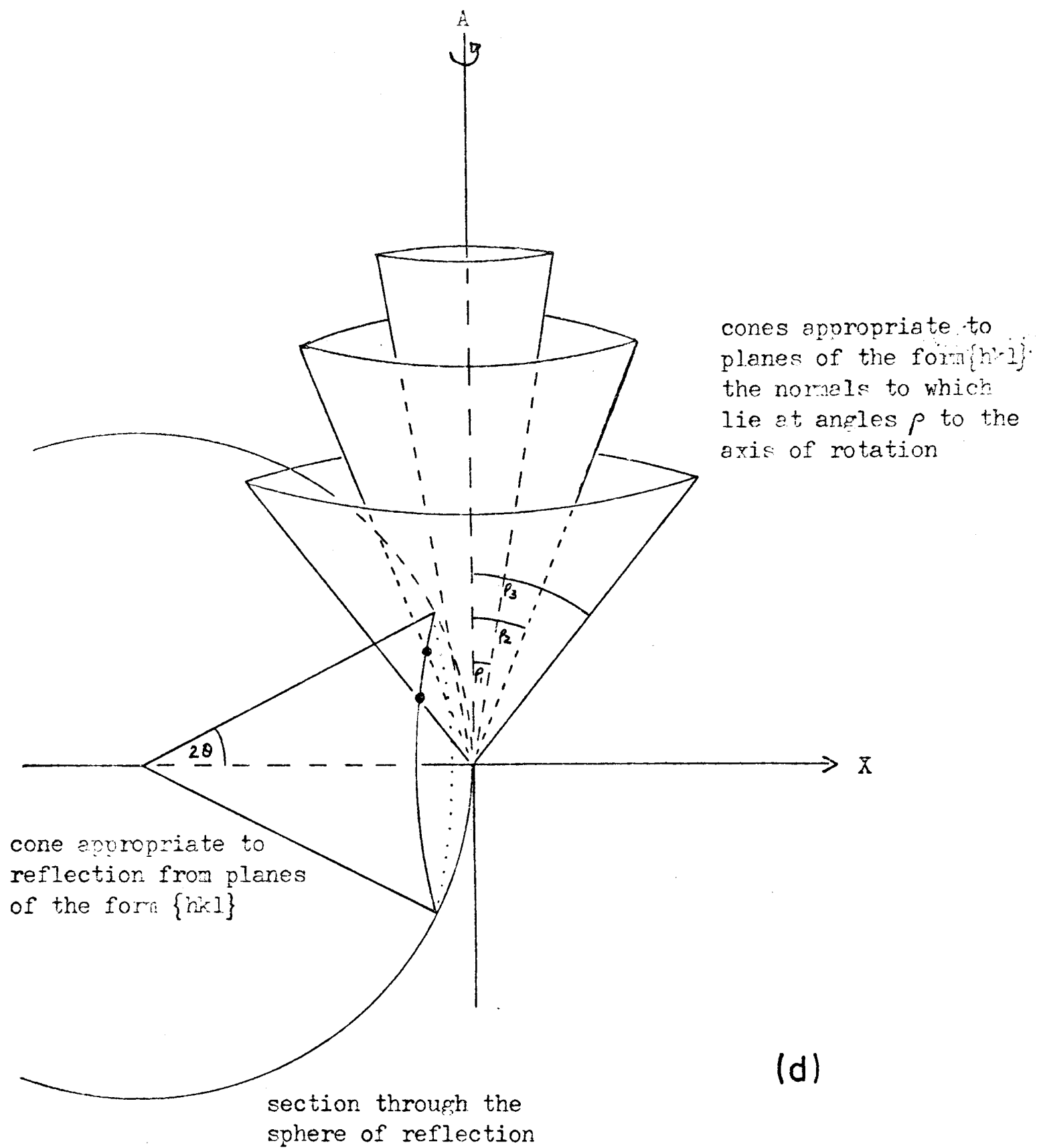
c) Location of the pole of the axis of rotation:

the intersection of small circles of appropriate radii, ρ centred on appropriate face poles give the pole, P of the axis of rotation

d) The condition for reflection to occur at particular angles

In all diagrams the axis of rotation is indicated by 'A' and the direction of the direct beam by 'X'.





The fibre photographs of Povlen-type chrysotile with well developed Debye arcs, while similar to the photograph of magnesite, differ in that the axial repeat indicated by the layer line spacing is normal ($\sim 5.3 \text{ \AA}$). Furthermore, the analogy between the diffraction effects just described from magnesite, and those from Povlen-type chrysotile, cannot be drawn too closely, as will be shown. In magnesite the unusual diffraction effects were shown to be dependent upon the multiplicity of the reflecting planes, which results from the relatively high symmetry of this mineral. Such is also the case with brucite, but in chrysotile the symmetry of the structure is much reduced from trigonal to orthorhombic or monoclinic, so that the effects of multiplicity, will accordingly be reduced. Nonetheless, in view of the marked similarity of the diffraction effects from these different minerals, it was thought worthwhile to attempt to interpret the Povlen-type chrysotile fibre photographs by the same method.

The extra first layer line reflections were assigned indices on the basis of previously indexed second layer reflections lying on the same Debye arcs. Following the same procedure as that adopted for magnesite the rotation axis was found to be perpendicular to the c-axis and at 60° to the a-axis; that is $\langle 110 \rangle$. The cell diagonal along $\langle 110 \rangle$ is of length $2a$ ($\sim 10.7 \text{ \AA}$), but because of centring odd order layer lines, based on a spacing of $\lambda/2a$, would be extinguished.

If, however, we merely stack individual layers, which possess hexagonal symmetry, with $\langle 110 \rangle$ parallel to the fibre axis, then unless some other feature of the resulting structure can be considered, we should expect no unusual diffraction effects.

2.3.2.2 A helical model for Povlen-type chrysotile

In fact there is an unusual aspect of the chrysotile structure which should be taken into account. The cylindrical nature of the structure necessitates complete azimuthal disorder between layers, in normal ortho- and clino-chrysotile the direction of disorder is circumferential, so that the a-axis lies perpendicular to this direction.

If we maintain this relationship, but orient layers so that $\langle 110 \rangle$ rather than $\langle 100 \rangle$ is now parallel to the fibre axis then the direction of disorder will lie along a high order helix, making an angle, δ_m of 60° with a plane perpendicular to the fibre axis.

On this basis we can construct what at first sight seems to be a possible fibre model for Povlen-type chrysotile. In order to account for the normal first and second layer reflections part of the fibre must consist of normal ortho-chrysotile. It is presumed that this constitutes the central portion, since a helical cylindrical structure entails some inevitable distortion which would be more easily accommodated by layers with larger radii. The presence of such 'additional' layers growing onto a normal fibre is in accord with the observation from electron microscopy that the fibrils are generally of greater diameter than usual.

In normal chrysotile the layers are stacked as though the atoms were smeared out circumferentially giving a set of parallel grooves and ridges which might be said to be arranged much as in a pile of tyres (Whittaker 1956a, b). In the helical model proposed the layers would again stack as though the atoms were smeared out parallel to the direction of disorder, so that in this instance, a fibre might be said to resemble a "fluted column".

The outer layers of such a fibril would have a helical structure similar to those treated by Whittaker (1955a), but would be unusual in that their b-axes would lie on helices of very high order. Layers of this type, in which the helices are at 60° to a plane perpendicular to the fibre axis would not be distinguishable from normal chrysotile by means of high resolution electron microscopy.

2.3.2.3 Diffraction theory for the helical model

Whittaker (1955a) considered diffraction by helical cylindrical lattices, in which the b-axes make only a small angle, δ_m with a plane perpendicular to the fibre axis. The geometric parameters used in the following discussion are those of Whittaker (1955a, b), they are given below and illustrated in figure 2.15 and 2.16.

a and b are the lattice parameters of the two-dimensional generating lattice.

α is the angle between the a and b axes.

β is a measure of the displacement between successive two-dimensional lattices, in a direction parallel to the fibre axis, but in the present discussion only cases for which $\beta = 90^\circ$ will be considered.

If the lattice shown in figure 2.16 were to be wrapped into a cylinder, so that instead of A_1 being joined to A'_1 , it were to be joined to (say) A'_3 or in the general case A_n were to be joined to A'_{n+N} then N can be said to be the order of the resulting helical lattice. The angle δ_m is then the angle between a plane perpendicular to the fibre axis and the b-axis of the m^{th} layer. The pitch of the helix, t can be derived from the relationship $a = \frac{t \cos \delta_m}{\sin \alpha}$. The number of b units in the "developed form of the generating lattice" is given by the expression -

$$p_m = \frac{2\pi mc \cdot \sin(\alpha + \delta_m)}{b \sin \alpha}$$

where c is the normal spacing between successive layers.

Whittaker (1955a) derived results for the anorthic cylindrical lattice of the second kind (Table 1.1), which can be used to predict results for all the helical circular lattices by substitution of appropriate values of α and β . Whittaker showed that the expression for the diffracted amplitude contained two terms, one involving zero order Bessel functions, the other non-zero order Bessel functions. The first of these terms (involving zero order Bessel functions) was split by Whittaker into summations with respect to n and v, within a summation with respect to m; m, v and n are a set of integers used to denote the co-ordinates of a lattice

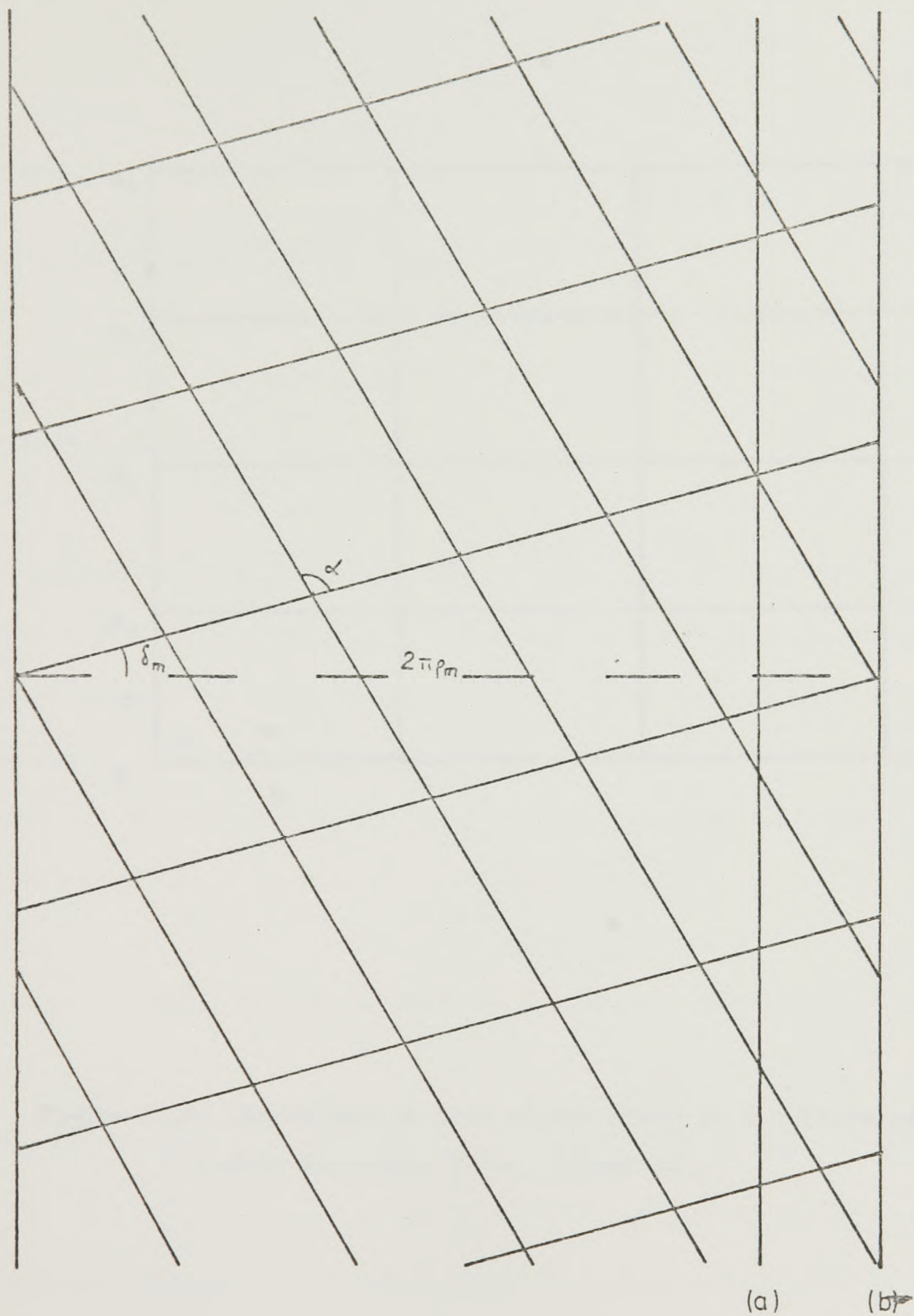


Figure 2.15. Generating lattice of a helical cylindrical lattice.

(a) Right hand boundary drawn as in Whittaker (1956c, fig.24)

(b) Corrected boundary

This diagram is for the case $N=1$.

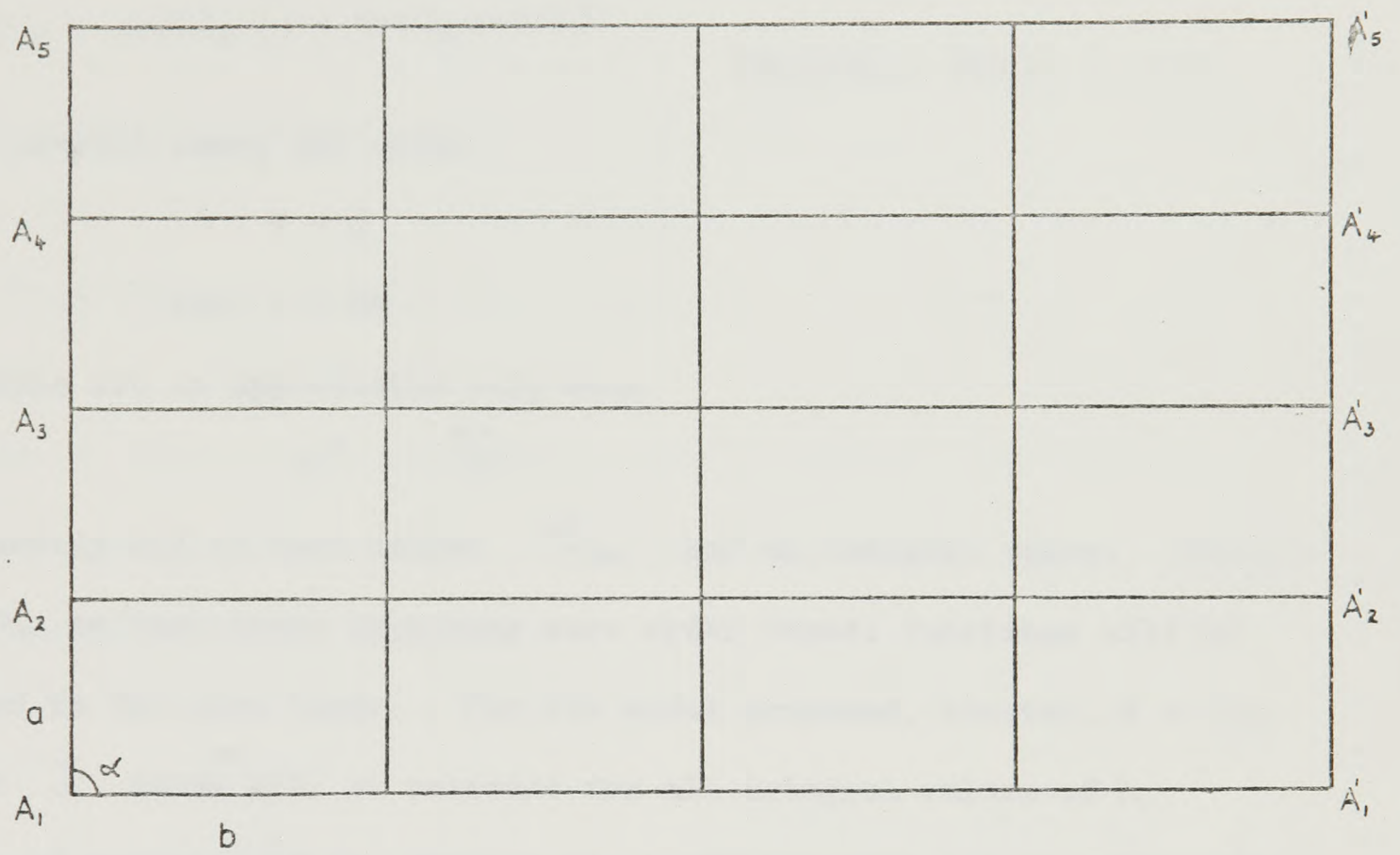


Figure 2.16. Generating lattice of one layer of a cylindrical lattice,
(after Whittaker 1956c, figure 10).

point: "the v^{th} lattice point on the n^{th} row of the generating lattice of the m^{th} cylinder" (Whittaker (1955a), p. 727). These summations can be expressed as -

$$\sum_n \exp \frac{2\pi i}{\lambda} x^* n t T \sin \beta \quad \text{Equation 2.6}$$

$$\sum_v \exp \frac{2\pi i}{\lambda p_m} x^* N t T \sin \beta \quad \text{Equation 2.7}$$

where $T = \cos^2 \delta_m (1 + \tan \delta_m \cot \alpha)$ (Whittaker 1955a, p. 727)

In the present case, for which

$$T = \frac{1}{4}$$

$$\text{and } t = 2a$$

Expression 2.6 is appreciable only near

$$x^* = \frac{h\lambda}{tT}$$

consequently 2.7 is zero unless $\frac{Nh}{p_m}$ has an integral value. Usually

$Nh \ll p_m$ so that terms involving zero order Bessel functions will be confined to the zero layer. For the model proposed, however, $N = 3p_m$ so that J_0 terms will be relevant for all integral values of h .

Because of centring of the lattice the condition that 2.6 be significant becomes -

$$x^* = \frac{2h\lambda}{tT}$$

Thus J_0 terms will occur on layer lines at ζ values given by

$$\zeta = \frac{4h\lambda}{a}$$

that is on the 0^{th} , 4^{th} , 8^{th} ... layer lines of 'normal' chrysotile

In fact the condition that Nh be a multiple of p_m will be satisfied by only one layer in the structure (because of distortions implicit in the helical structure), for which $\delta_m \approx 60^\circ$ and N is exactly $3p_m$. For all other layers N will only approximate $3p_m$ so that J_0 terms will arise from a single layer, and we would expect such reflections to be very diffuse and weak. The term involving non-zero order Bessel functions, J_q ,

will be significant on layer lines for which

$$\xi = \frac{h\lambda}{c} \pm \frac{K\lambda}{b} \sec \delta_m \cot (\alpha + \delta_m) \quad \text{Equation 2.8}$$

and when

$$q = K p_m \mp N h$$

(Whittaker 1955a, p. 728)

For $\delta_m = 60^\circ$ and $\alpha = 90^\circ$ 2.8 becomes

$$\xi = \frac{h\lambda}{c} \mp \frac{4K\lambda}{c}$$

Reflections of the type h0l will therefore occur at

$$\xi = \frac{h\lambda}{2a}$$

and the order of the Bessel function, given by q will be Nh. Reflections of this type with h = odd will be extinguished by centring so that h0l reflections will lie on layer lines spaced at λ/a corresponding to even values of h. In particular, when h = 2 then J_{2N} terms will occur at the same ξ value as the first layer line of 'normal' chrysotile.

The positions of such reflections will depend upon the maxima of the Bessel functions involved -

$$J_{Nh} \left(\frac{2\pi}{\lambda} \xi m c \right)$$

Now,
$$N = \frac{2\pi m c}{2a} \tan \delta_m$$

$$= \frac{3\pi m c}{b} \quad \text{when } \delta_m = 60^\circ$$

and the Bessel function will be of negligible value until $\xi = \frac{3h}{2} \cdot \frac{\lambda}{b}$.

Thus for h = 2 the function will not attain appreciable values until $\xi = 3b^*$, in accord with the observation that the extra reflections on the first layer line of Povlen-type chrysotile, lie to the high angle side of the normal position of the 130 reflection.

These extra reflections might therefore be explained by diffraction from a structure of the type proposed, provided that the positions of the maxima of $\sum_m J_{Nh} \left(\frac{2\pi m c}{\lambda} \xi \right)$ - when h = 2 - are at the values of ξ appropriate to 20l reflections occurring on the normal first layer line.

Before discussing the positions at which reflections for which $K \neq 0$ will be expected to occur, it is necessary to correct an error in the earlier work of Whittaker (1955a, 1956c). This error arose from a mistake in figure 24 of Whittaker (1956c), which involved the incorrect drawing of the right hand boundary of the generating lattice for an anorthic cylindrical lattice of the second kind (helical lattice); this in turn led to an erroneous use of ρ_m (see above for the definition of this parameter). The original and corrected versions of the diagram are illustrated in figure 2.15.

In general -

$$\frac{\rho_m b}{\sin(\alpha + \delta_m)} = \frac{2\pi \rho_m}{\sin \alpha}$$

Also:

$$\frac{Nt}{2\pi \rho_m} = \tan \delta_m$$

So that

$$\rho_m = \frac{Nt \sin(\alpha + \delta_m)}{b \sin \alpha \tan \delta_m}$$

If this value of ρ_m is inserted into the expression -

$$Z^* = \frac{h\lambda}{t} \pm \frac{K\rho_m U\lambda}{NtT}$$

(from Whittaker (1956c) p. 161 line 5).

Where T and U have the meanings given by Whittaker (1956c, p. 160)

$$\text{then} \quad \delta = \frac{h\lambda}{t} \pm \frac{K\lambda \cos(\alpha + \delta_m)}{b \sin \alpha} \quad \text{Equation 2.9}$$

$$\text{rather than} \quad \delta = \frac{h\lambda}{t} \pm \frac{K\lambda}{b} \cdot \sec \delta_m \cdot \cot(\alpha + \delta_m) \quad \text{Equation 2.8}$$

This error is of no consequence when $K = 0$ and was therefore not discussed earlier. It also has a negligible effect when δ is small, as in the circumstances originally discussed by Whittaker, but for the present model in which $\alpha = 90^\circ$ and $\delta = 60^\circ$ it has a major effect and equation 2.9 becomes -

$$\delta = \frac{h\lambda}{t} \pm \frac{K\lambda}{2a}$$

For the model proposed $t = 2a$ (see above), so that reflections for which $K \neq 0$ can be regarded as being shifted onto layer lines at

$\xi = \frac{h\lambda}{2a}, \left(= h \frac{a^*}{2} \right)$ and then split above and below these layer lines, to a degree dependent upon the value of $\pm \frac{K\lambda}{2a}, \left(= K \frac{a^*}{2} \right)$. Since these reflections are split by multiples of $a^{*/2}$ from layer lines occurring at multiples of $a^{*/2}$ their resultant positions will be at ξ values appropriate to the layer lines of normal chrysotile.

The positions of the reflections along the layer lines will depend upon Bessel functions of the type $J_q \left(\frac{2\pi}{\lambda} \xi m c \right)$,

where $q = K p_m \mp N h$ (see above). For the present model $N = 3 p_m$

so that the order of the Bessel function, $q = p_m (K \mp 3h)$. Also

$p_m = \frac{\pi m c}{b}$ so that the argument of the function, $\frac{2\pi}{\lambda} \xi m c$

can be expressed as $\xi \frac{2b}{\lambda} p_m$. Thus the Bessel function will not

attain appreciable value until $p_m (K \mp 3h) = \xi \frac{2\pi}{\lambda} p_m$

i.e. until $\xi = \frac{K \pm 3h}{2} b^*$.

When this expression for ξ is solved it is found that the reflections for which $K \neq 0$ will occur at positions at which reflections from normal chrysotile are to be expected. Thus for the present helical model not only will such reflections occur on layer lines appropriate to normal chrysotile but also they will occur at positions along those layer lines consistent with reflections from normal chrysotile. A few examples are given below -

Reflection	Positions of the two components of the split reflection in terms of normal chrysotile reflections
020	110 : $\bar{1}10$
060	330 : $\bar{3}30$
110	$1\bar{1}0$: 020
130	200 : $\bar{1}30$
310	$2\bar{4}0$: 150
330	$3\bar{3}0$: 060

2.3.2.4 Breakdown of the helical model

The diffraction effects predicted for the proposed model are in accord with the features observed in both x-ray fibre photographs taken with Cu radiation and in the corresponding layer lines of the electron diffraction patterns. If higher order layer lines than the second are considered, however, certain shortcomings are apparent.

The diffraction effects to be expected from helical structures have also been discussed, in the context of investigations into the structure of proteins (Cochran, Crick and Vand, 1952; Franklin and Klug, 1955). Cochran et al (1952, p. 586) noted "the property of Bessel functions ... that for small values of the argument $2\pi Rr$ the function $J_n(2\pi Rr)$ is very small when n is large. The greater the value of n , the greater $2\pi Rr$ can be before $J_n(2\pi Rr)$ becomes appreciable."

In the present instance, as a consequence of this feature of Bessel functions, we would expect reflections due to Bessel functions of higher orders to occur at greater values of ξ . Thus as higher layer lines were observed a 'meridional gap' would appear and this gap would widen toward higher order layer lines. Such a meridional gap is not apparent in the electron diffraction patterns, which pointed to the need to consider the features of layer lines not visible on the usual fibre photographs taken with Cu radiation.

On layer three (for which $h = 6$) we would expect, on the basis of the model proposed, reflections due to Bessel functions of orders, $Nh = 6N$. These functions would not attain appreciable values until $\xi = 9b^*$. On examination of the third layer line on the electron diffraction patterns a set of sharp reflections following the 330 reflection is apparent. Similar reflections were also observed on an equi-inclination photograph, taken with Zr-filtered Mo radiation. Unlike the sharp reflections following the 130 reflection on the first layer line these reflections cannot be explained in terms of the model proposed. Sharp reflections on the fifth and seventh layer lines of the electron diffraction patterns, following the 150 and 170 reflections respectively present the same problem.

These difficulties would seem to rule out the proposed helical model for Povlen-type chrysotile.

2.3.3. Development of a model with flat layers

2.3.3.1. The need for partial ordering

It seems that there is little alternative but to index the extra reflections of the first layer line of Povlen-type chrysotile fibre photographs with indices of 13l type. In so doing we accept a degree of ordering in the b-axis direction. This must involve a departure from the normal cylindrical structure, although we cannot adopt a lath-like model for Povlen-type chrysotile in view of the observation, with the electron microscope, of fibrils less than 1000 Å diameter showing rotational symmetry.

If ordered stacking of layers is invoked to permit the presence of 13l type reflections then we might expect other hkl reflections to occur; for example a series of 11l and 15l reflections following 110 and 150 respectively. Reference to figure 1.1 suggests, however, that the relationship between the uppermost, octahedral hydroxyls and the basal oxygens of the next layer will not be particularly sensitive to random displacements of $\pm \frac{nb}{3}$. Such displacements would explain the absence of hkl reflections for which $k \neq 3n$, in addition to the absence of those for which $h+k \neq 2n$, a condition imposed by centring of the lattice.

2.3.3.2 A polygonal model

In some of the electron diffraction patterns the tails of the 110 reflections (and to a less noticeable extent the tails of other h10 reflections) present a more uneven profile than is usual. This "lumpiness" is on a coarser scale than the fine structure of hk0 reflections sometimes observed in electron diffraction of single fibrils (Whittaker and Zussman, 1971), previously referred to in section 2.1 and in chapter one. On the other hand these subsidiary intensity maxima are irregularly spaced and cannot be interpreted in terms of 11l type reflections. Rather, this feature is taken to suggest an imperfect rotational symmetry, such as would arise from a polygonal fibre.

It is suggested that the thickness of coherent structure in the Z^* direction is limited to single serpentine layers. The $hk0$ reciprocal lattice points are therefore extended into rods lying parallel to Z^* , and modulated by the structure factor of an individual layer. Normally, because of the cylindrical structure of chrysotile fibres, such rods can be envisaged as being smeared out into discs, which are non-uniform in character in a radial direction. Thus intersection with the sphere of reflection will give rise to a smoothly varying intensity profile.

In the case of a polygonal structure, however, a limited number of intersections of the sphere with reciprocal lattice rods will occur. Thus, a series of spots, rather than a smooth tail will result. The arrangement of these spots will depend upon the number of sides in the polygon and on its regularity. There seems to be no reason to expect either a regular or symmetrical distribution of spots.

In the case of an x-ray fibre photograph the presence of many fibres in random orientation about the x-axis will result in this spottiness of $h10$ reflections being smoothed out.

It seems from some of the diffraction patterns that some part of the Povlen-type chrysotile fibres consists of normal, cylindrical chrysotile. This is inferred from observation of the profiles of $hk0$ reflections (and their tail regions), which appear to involve a smoothly varying component, on which are superimposed (where appropriate) $h3l$ reflections. In x-ray diffraction this smoothly varying component may simply be due to normal fibres within the fibre bundle. However, some of the electron diffraction patterns, from what are taken to be single fibrils, also indicate the presence of cylindrical chrysotile.

It is suggested that the cylindrical layers, when present, may constitute the central portion of a fibril, while polygonally arranged flat layers have grown as an "outer shell". There is no definite reason why such a model should not be "turned inside out", with polygonally arranged layers forming the core of the fibre. However, it seems more reasonable that the

structure should pass, outward from the centre, from slightly curved cylindrical layers of large radius to flat layers growing polygonally, than that the reverse should be true. Furthermore this arrangement would provide more scope for the development of a many-sided polygonal structure: layers must be present on sides in a sufficient variety of azimuths about the fibre axis to account both for the general appearance of rotational symmetry in the electron diffraction patterns, and for the close spacing of the diffraction maxima in the tails of the 110 reflections.

The model developed in this section is illustrated diagrammatically in figure 2.17, and the indices assigned - on the basis of this model - to the reflections observed, are given in Table 2.2.

2.3.3.3 Layer stacking in the polygonal model

The model proposed can account for the positions of the reflections observed in x-ray and electron diffraction of Povlen-type ortho- and clino-chrysotile specimens. The relative intensities of the reflections, and the structural implications of these are now considered. Whittaker (1953b, 1956a, b) showed that in both the clino- and ortho-chrysotile structures the layers are stacked as though the atoms were smeared out into corrugations running circumferentially, parallel to the b-axis. Mutual register of layers in the a-axis (fibre axis) direction is maintained by the O₁ atoms, lying at the base of the tetrahedral layer, which fit into the grooves between the uppermost hydroxyl groups of the layer below. This relationship between layers in the stacking sequence is achieved by a shift, Z, between successive layers, parallel to the a-axis.

The structure proposed for Povlen-type chrysotile implies essentially flat layers, as distinct from cylindrical layers, and in this sense is akin to lizardite and the six-layer ortho-serpentine (and other multi-layer serpentines) which can probably be regarded as polytypes derived by various stacking sequences of the same, basic serpentine layer. Considering the necessary rotational symmetry of the model on the other hand, its affinities are with chrysotile, rather than lizardite which is essentially platy (Zussman et al, 1957; Whittaker and Zussman, 1971).

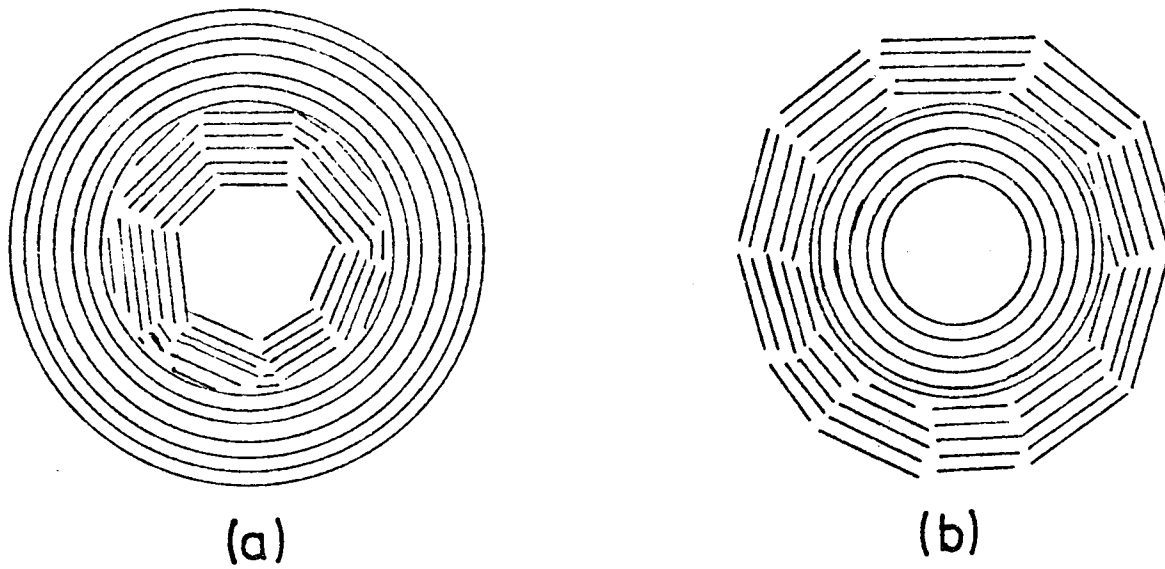
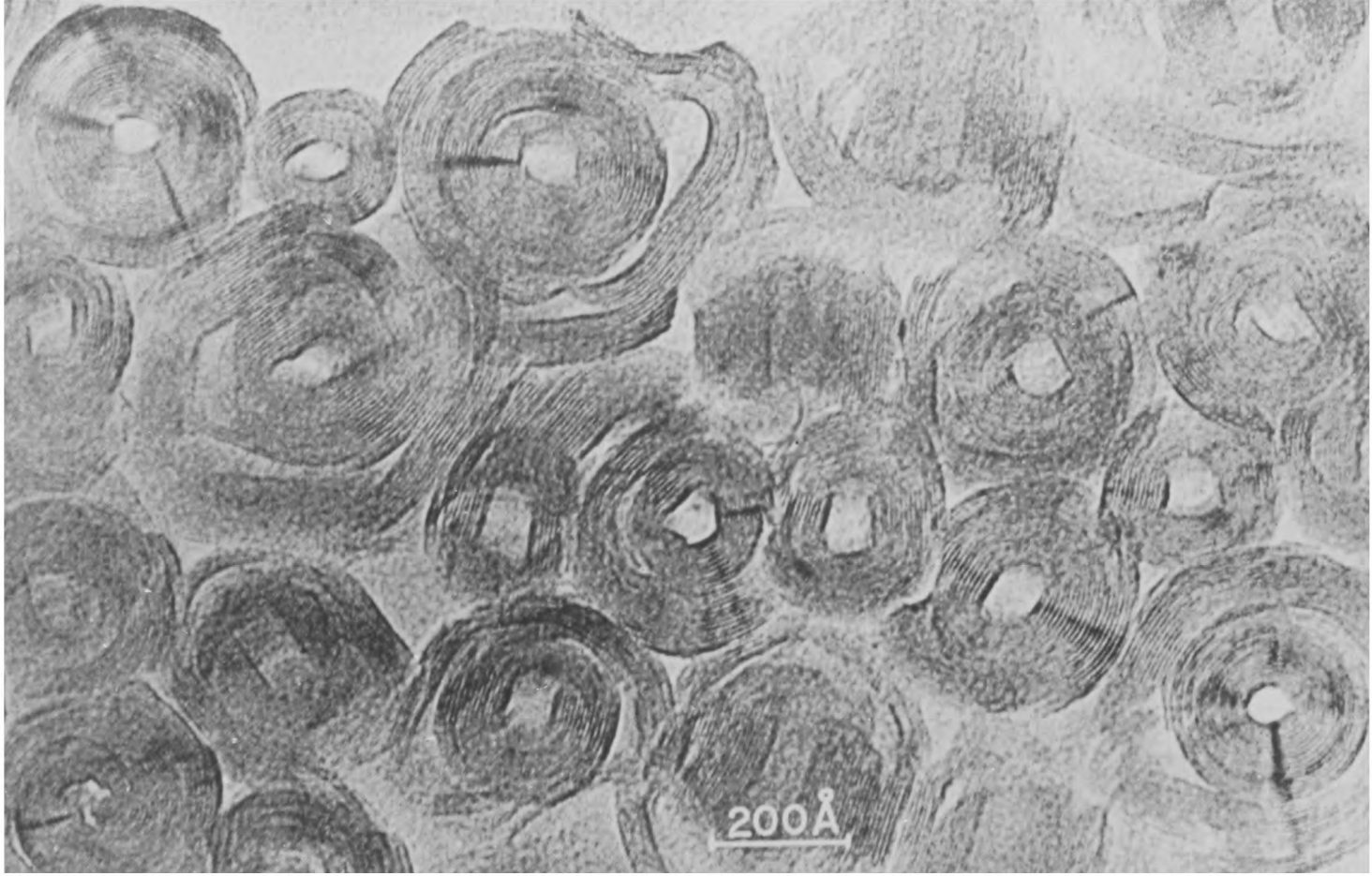


Figure 2.17. (a) and (b). Schematic representations of possible growth models for Povlen-type chrysotile; (b) is thought to be the more likely. (c) -overleaf- chrysotile showing evidence of polygonal growth, in a specimen from Tasmania (Yada 1971, figure 11).



(c)

It was thought that the stacking of the layers in Povlen-type chrysotile might be similar to that of lizardite rather than chrysotile - the major distinctions between the stacking in these two polymorphs concerns the magnitude of the shift, Z, between layers; (for lizardite this shift is zero) and the resultant relationship of basal oxygens and octahedral hydroxyls. Although the 201 type reflections of Povlen-type chrysotile cannot be indexed on the basis of a one-layer cell (i.e. $c \approx 7.3 \text{ \AA}$) as is the case with lizardite (Whittaker and Zussman, 1956), this does not altogether rule out any possible comparison.

Rucklidge and Zussman (1965) found that the stacking sequence of lizardite from Kennack Cove, Cornwall - which is exceptional insomuch as its crystallite size is sufficient to permit the meaningful application of single-crystal x-ray methods - included both one layer ($\mu\mu\ldots$ and $\delta\delta\ldots$)* and two layer ($\mu\delta\mu\delta\ldots$)* domains. It is shown below, that in fact, the stacking in Povlen-type ortho-chrysotile (but not in Povlen-type clino-chrysotile) can be likened to that of the two layer domains of lizardite.

Whittaker (1956b, c) calculated the intensities of the h0l reflections of ortho-chrysotile as functions of the type

$$|F_c|^2 = A + B \sin 2\pi h Z + C \cos 2\pi h Z$$

(Whittaker 1956b, p. 863).

and plotted these graphically (1956c).

Z is the interlayer shift previously mentioned.

By comparison of the observed and calculated values he was able to determine the best value of Z for ortho-chrysotile as 0.441. The intensities of 201 reflections from Povlen-type ortho-chrysotile (Table 2.5) differ significantly from those calculated by Whittaker for these reflections. In particular the 207 and 209 reflections are rather weak.

* μ and δ were used by Rucklidge and Zussman, to refer to the different types of serpentine layer, which arise from the occupation of two alternative sets of three positions by Mg atoms in the octahedral layer (Whittaker, 1956a).

TABLE 2.5

Comparison of the observed intensities of 20l type reflections of Povlen-type ortho-chrysotile with those calculated for various models

hkl	I _{obs}	1	2	3	4
201	23	12	35	11	6
202	100	100	65	100	100
203	35	36	100	30	56
204	22	17	23	25	14
205	39	36	13	38	36
206	16	12	31	10	12
207	17	20	44	23	33
208	19	21	3	9	8

- 1.) Intensity values given by Bailey (1969, Table 3) for model (2H₁)
- 2.) Intensity values given by Bailey (1969, Table 3) for model (20r)
3. Intensity values calculated from $|F_c|^2$ values for Z = 0, read from graphs given by Whittaker (1956c, figures 55 and 56).
4. Intensity values calculated from $|F_c|^2$ values given by Whittaker (1956b, Table 2) for ortho-chrysotile (Z = 0.441).

Note - all sets of values have been recalculated to make the intensity of the strongest reflection in the series equal to 100.

Several stacking schemes for the trioctahedral 1:1 layer silicates have been proposed. Those put forward by Steadman (1964) and Zvyagin (1967) were compared and discussed in some detail by Wicks (1969 pp. 20-33). Mention was also made in that discussion of the treatment by Bailey (1967) of stacking in the serpentine minerals. In a more recent paper Bailey (1969) has presented a fuller account of his proposed stacking scheme for the 1:1 trioctahedral layer silicates. In view of the full discussion already presented by Wicks (1969), and the general similarity of these various stacking schemes detailed comparison is not undertaken here.

In all of the above mentioned schemes the author made at the outset, certain simplifying assumptions concerning the composition and geometry of the layers, and the ways in which they may be stacked. In particular, it was assumed that the relative positions of successive layers are limited by the requirement for hydrogen bonding, between the basal tetrahedral oxygens of one layer and the upper octahedral hydroxyls group of the layer below (a relationship suggested by Hendricks, 1938).

Bailey (1969) derived twelve different polytypes, plus a further four enantiomorphs. He presented structure amplitude factors for the stronger reflections, and calculated powder patterns for the twelve polytypes. Bailey assumed a composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and cell dimensions appropriate to aluminous serpentines. Most natural crystals will not obey all of Bailey's assumptions, so that in practice the stacking will often be more complex. The agreement between observed and calculated intensities will accordingly, be imperfect.

Nonetheless it was thought worthwhile to compare the structure amplitudes given by Bailey with the intensities observed on the fibre photographs. The best match (after consideration of the effects of the Lorentz factor), was with Bailey's group D. Comparison of a wider range of reflections indicated 2H, as the model which most nearly satisfies the data. This model is derived by direct super-position of layers, related to each other by a rotation of 180° : that is, a sequence of μ and δ

type layers in which the alternative Mg positions are occupied in alternate layers. This differs from normal ortho-chrysotile in that the interlayer shift, Z is zero rather than 0.441.

The observed intensity profile would be expected to be intermediate between those for $Z = 0$ and $Z = 0.441$, since the model proposed requires the presence of normal ortho-chrysotile, as well as the differently stacked, polygonally arranged layers. In Table 2.5 intensity data for various stacking models are compared with the observed intensities, from Povlen-type ortho-chrysotile.

Povlen-type clino-chrysotile, on the other hand seems to be stacked in the same manner as normal clino-chrysotile, except that there is ordering in the b-axis direction. The intensities of the 20l reflections on fibre photographs show no marked differences from those of normal clino-chrysotile. The absence of all hkl reflections for which $k \neq 3n$ is taken to indicate random displacements of $\pm \frac{nb}{3}$ between layers, as in Povlen-type ortho-chrysotile.

2.3.4 Conclusion

A model, illustrated in figure 2.17 is proposed to account for the unusual diffraction effects from the so-called Povlen-type chrysotiles. The model involves partially ordered stacking of essentially flat layers, arranged in a polygonal fashion, possibly around a core of normal cylindrical chrysotile. The manner in which the layers are stacked together differs between Povlen-type ortho- and clino-chrysotile.

The model proposed accounts for the observed diffraction effects. Verification could perhaps be achieved by high resolution electron microscopy of fibre samples sectioned perpendicular to the fibre axis. Figure 2.17c (after Yada, 1971) suggests that polygonally arranged layers can occur, though Yada does not mention any unusual diffraction effects from this particular sample. Observation with a scanning electron microscope is not likely at the present, to provide the resolution required.

TABLE 2.6

Comparison of the observed positions of "humps" in the profile of the 130 reflection of clino-chrysotile with the calculated and observed positions of 131 type reflections of Povlen-type clino-chrysotile

co-ordinates of observed 'humps' *	Calculated of 131 type reflections**	co-ordinates of 131 type reflections***	Observed co-ordinates of 131 type reflections***	hkl
($\text{\AA}^{-1}$)	($\text{\AA}^{-1}$)	($\text{\AA}^{-1}$)	($\text{\AA}^{-1}$)	
0.331	0.325	0.33	130	
0.360	0.357	0.36	132	
0.399	0.390	0.40	133	
0.438	0.432	0.44	134	

* Specimen number G400

** Calculated assuming cell parameters as follows -

$$a = 5.34 \text{ \AA}$$

$$b = 9.24 \text{ \AA}$$

$$c = 14.63 \text{ \AA}$$

$$B = 93^{\circ} 16'$$

*** Specimen number G148.



Figure 2.18. Observed profiles of the 130 reflection of chrysotile.

(a) Smooth profile (clino-chrysotile, specimen G218)

(b) 'Bumpy' profile (clino-chrysotile, specimen G435)

(c) Povlen-type clino-chrysotile, specimen G148

2.4 Chrysotiles intermediate between normal and Povlen-type

A feature commonly observed on fibre photographs of chrysotile is that "... the tail of the 130 reflection ... is divided into partly resolved diffuse "humps", while on others it is quite continuous and appears to have a monotonic distribution of intensity." Whittaker (1956c, p. 312). The 110 reflection is not affected by the same variability. Whittaker considered that the 130 reflection was more likely than the 110 reflection to be sensitive to atomic co-ordinates, and fibril size and size distribution. He also pointed out that the appearance of partially resolved "humps"^{was} similar to what would be expected if there were a transition towards a three dimensionally ordered structure.

Several fibre photographs of chrysotile showing "lumpy" 130 reflections have been examined, and the positions of the diffuse intensity maxima measured with a Bernal chart. The values obtained and the overall profiles are very similar to those of the series of reflections indexed as 13l's on photographs of Povlen-type clino-chrysotile. No photographs were examined which showed 130 profiles which could be matched with Povlen-type ortho-chrysotile, though this is not surprising in view of the rarity of specimens with high ortho-chrysotile content.

It seems then, that the variable character of the 130 reflection may be attributed to limited regions, variable in extent, of the fibre bundle in which the stacking of layers is similar to that in Povlen-type clino-chrysotile. The calculated[§] values of 13l reflections from Povlen-type clino-chrysotile are compared with the observed [§] values of the diffuse maxima, in Table 2.6. In figure 2.18 are shown several 130 reflection profiles which range from smooth, through increasingly lumpy character to Povlen-type.

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CHAPTER THREE

The nature of Para-chrysotile

3.1 Introduction

In this introductory section a brief account will be given of the nature of para-chrysotile and of previous observations of this variety of chrysotile.

Fibre photographs of chrysotile commonly show weak reflections defining subsidiary layers lines, which indicate a fibre axis repeat of $\sim 9.2\text{\AA}$. Aruja (1943) suggested that these spots could be attributed to the diffuse reflections arising from material having the same structure as chrysotile, but with the $\langle \bar{0}10 \rangle$ or $\langle \bar{1}30 \rangle$ axis parallel to the fibre axis (see Whittaker and Zussman, 1956). Hargreaves and Taylor (1946) found that the component giving rise to the reflections on subsidiary layer lines could be removed by prolonged extraction with water. This led them to suggest that this material might consist of layers stacked in a less orderly manner than in chrysotile.

A more detailed structural interpretation was presented by Whittaker (part I of Whittaker and Zussman, 1956; Whittaker, 1956a). This study was made possible by the availability of specimens containing a higher proportion of this component, so giving rise to photographs displaying more reflections than had previously been observed. The name "para-chrysotile" was applied to this material by Whittaker and Zussman.

The measured co-ordinates and the indices assigned to the reflections detected by Whittaker are given in Table 3.1. It was demonstrated that the diffraction effects observed could be explained in terms of a helical cylindrical lattice. The structure inferred by Whittaker is closely analogous to that of ortho-chrysotile, but with the $9.2\text{\AA}$ b-axis, rather than the a-axis ($\sim 5.5\text{\AA}$) lying parallel to the cylinder axis.

TABLE 3.1

Positions of para-chrysotile reflections, after Whittaker (1956a)

Layer line	Position		Indices*
	1	2	
Zero	0.614	0.398	200
First	0.307	0.199	110
	0.889	0.577	310
	1.482	0.961	510
Second	0	0	020
Third	0.28-0.37	0.18-0.24	130
	0.873	0.566	330
	1.472	0.955	530
Fourth	0	0	040
	0.600	0.389	240
Sixth	0.017	0.011	060
	0.106	0.069	061
	0.211	0.137	062
	0.311	0.202	063
	0.413	0.268	064
	0.530	0.344	065
	0.606	0.393	260
	1.168	0.758	460

1. Values of $\bar{f}$ given by Whittaker, based upon measurement of films taken with CuK_α radiation.

2. Values of $\bar{f}$ ($\text{\AA}^{-1}$), calculated from 1.

Cell parameters* - $a \approx 5.3 \text{ \AA}$
 $b = 9.24 \pm 0.02 \text{ \AA}$
 $c = 14.7 \pm 0.1 \text{ \AA}$

* h and l indices (and a and c cell parameters) of Whittaker have been transposed to accord with the axial convention which is now generally accepted.

The direction of disorder is therefore in the a-axis direction, so that no reflections of the types h0l or hkl are to be expected and reflections of the types hk0 and h00 will be diffuse. It was further shown that the layers stack together in a manner analogous to that in other varieties of chrysotile. Random displacement of $\pm \frac{nb}{6}$ between adjacent layers were considered likely by Whittaker, and to account for the absence of Okl reflections for which $k \neq 6n$.

Observation of dispersed fibre samples in the electron microscope affords the opportunity to obtain the diffraction effects from single fibrils and hence to observe the fibre diffraction pattern from isolated para-chrysotile, a result which - as was pointed out in chapter one - is unlikely to be achieved by x-ray diffraction of fibre bundles.

Para-chrysotile fibrils are, however, relatively unusual and even in the electron microscope are rarely observed in isolation. Honjo and Mihama (1954) reported that only one fibre out of the fifty which they observed gave a diffraction pattern indicating material in this orientation, and Shitov and Zvyagin (1966) stated that -

"In a number of cases the para form of chrysotile was observed, and here it was particularly remarkable that these specimens were found in combination with clino and ortho forms of chrysotile, in individual tubular crystals selected for diffraction."

(Shitov and Zvyagin, 1966, p. 714).

Honjo and Mihama did not publish the para-chrysotile electron diffraction pattern, nor did they report any attempt to index the reflections. Shitov and Zvyagin on the other hand, published two electron diffraction patterns from "composite tubular crystals" which show reflections due to para-chrysotile, associated in the one instance with ortho-chrysotile, in the other with clino-chrysotile. In both patterns (which are poorly reproduced in the publication) all reflections are somewhat diffuse,

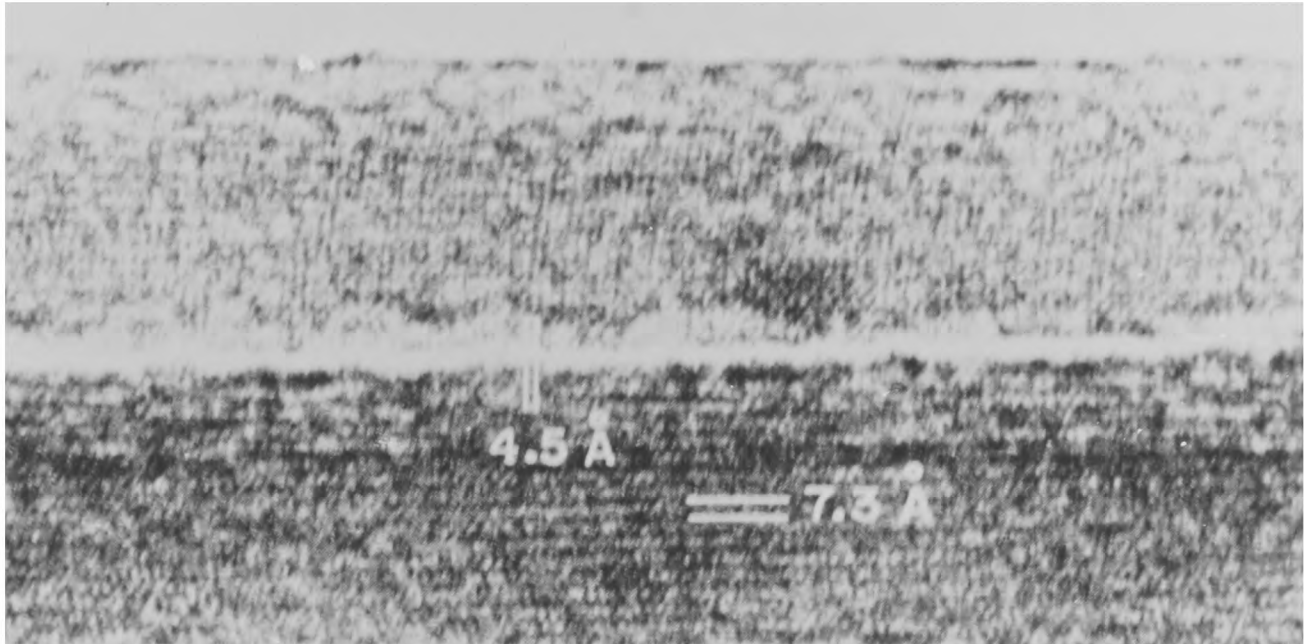


Figure 3.1. High resolution electron micrograph of para-chrysotile, after Yada (1967, figure 6). The transverse lattice fringes corresponding to a spacing of $\sim 4.5 \text{ \AA}$ are clearly resolved.

indicating that in both fibrils the two varieties are of limited radial extent. The pattern derived from para-chrysotile and ortho-chrysotile closely resembles that published by Zvyagin (1967) although it is not explicitly stated by Zvyagin to be the source.

An electron micrograph of a para-chrysotile fibre was published by Yada (1967) and is reproduced as figure 3.1. In this micrograph the 020 lattice fringes, spaced at $\sim 4.5\text{\AA}$ lie perpendicular to the fibre length. Little information can be derived from this micrograph concerning the fibril dimensions, and Yada reports that his high resolution studies did not confirm whether para-chrysotile possesses a cylindrical structure or is simply a curved crystallite. Yada mentioned further observations of para-chrysotile in a later paper (Yada, 1971), but in neither publication did he reproduce any diffraction patterns or give any diffraction data from para-chrysotile fibres.

3.2 Present observations of para-chrysotile

3.2.1 Introduction

During the examination in the electron microscope of fibres taken from a slip-fibre* brucite vein (sample number AG 67.761, from the Jeffrey mine, Quebec) numerous chrysotile fibres were also observed. Several of these were found, from their electron diffraction patterns, to contain para-chrysotile (see figures 3.2 and 3.3). In one instance diffraction pattern arising solely from para-chrysotile was obtained (figure 3.4).

As well as intergrowths of para-chrysotile with ortho and clino-chrysotile, parallel intergrowth with brucite was also observed - the features of these intergrowths are discussed in chapter four. In this vein sample

* The term slip-fibre is used to distinguish fibrous veins in which the fibres lie approximately parallel to the vein walls from those in which the fibres are almost perpendicular to the walls.

TABLE 3.2

Positions of para-chrysotile reflections observed in
electron diffraction, and proposed indices

<u>Layer line</u>	<u>$\xi (\text{\AA}^{-1})$</u>	<u>Proposed indices</u>
Zero	0.14	002
	0.28	004
	0.39	200, 201
	0.41	006, 202
	0.43	203
	0.47	204
	0.56	008, 206
	0.77	400
	0.84	0.0.12
First	0.20	110
	0.59	310
Second	0	020
Third	0.19	130
	0.24	132
	0.27	133
	0.33	134
	0.38	135
	0.46	136
	0.57	330, 138
	0.72	1.3.10
Fourth	0	040
	0.39	240

TABLE 3.2 (Contd.)

<u>Layer line</u>	<u>ξ ($\text{\AA}^{-1}$)</u>	<u>Proposed indices</u>
Sixth	0	060
	0.07	061
	0.15	062
	0.28	064
	0.40	260
	0.57	068
Eighth	0	080
Ninth	0.20	190
	0.23	192
	0.34	194
	0.58	390
Tenth	0	0.10.0
Twelfth	0	0.12.0

Indices assigned on the basis of orthorhombic unit cell -

$$a = 5.3 \text{ \AA}$$

$$b = 9.24 \text{ \AA}$$

$$c = 14.7 \text{ \AA}$$

the abundance of para-chrysotile seems to be somewhat greater than is normal in chrysotile samples, though even here it is far from common and attempts to obtain an x-ray fibre photograph of a fibre bundle rich in para-chrysotile were not successful.

The diffraction results obtained during the present studies will for the most part, be presented in the form of a comparison with the results reported from x-ray fibre diffraction patterns by Whittaker (1956a). For convenience the discussion will be arranged under two headings; even order layer lines and odd order layer lines. The co-ordinates of the reflections observed, together with the proposed indices are given in Table 3.2.

The electron diffraction pattern in figure 3.2 shows weak reflections on layer lines appropriate to ortho or clino-chrysotile. The hol reflections on the even order layer lines are streaked along the layer line (this is particularly noticeable on the second layer line) to an extent which indicates that the layer stacking must be disordered, and it is not possible therefore to make the usual distinction between ortho- and clino-chrysotile. On odd order layer lines splitting of the diffuse hko reflections can clearly be seen, and indicates a helical cylindrical lattice. The presence of ortho-chrysotile can be established by examination of the appropriate layer lines of the diffraction pattern in figure 3.3.

3.2.2. Even order layer lines

The 001 reflections due to para-chrysotile coincide with similar reflections deriving from ortho- and clino-chrysotile. Consequently, in the photographs examined by Whittaker (which showed para-chrysotile as only a minor component in the fibre bundle), the presence of the 001 reflections of para-chrysotile could only be inferred. The validity of this inference is confirmed by the electron diffraction patterns in which a series of basal reflections similar to that normally obtained from ortho- or clino-chrysotile, can be observed on the zero layer line.

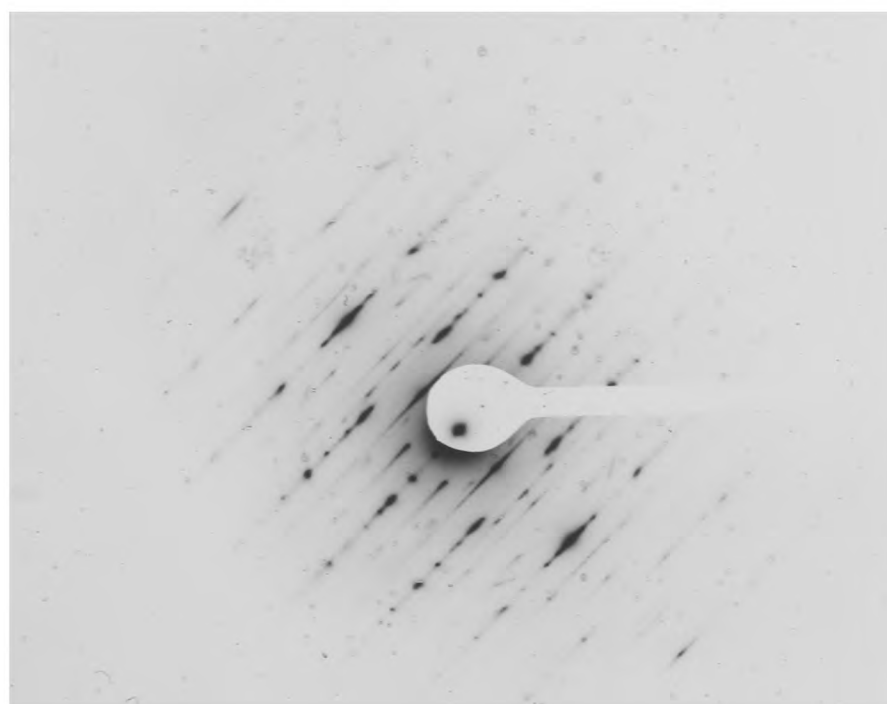
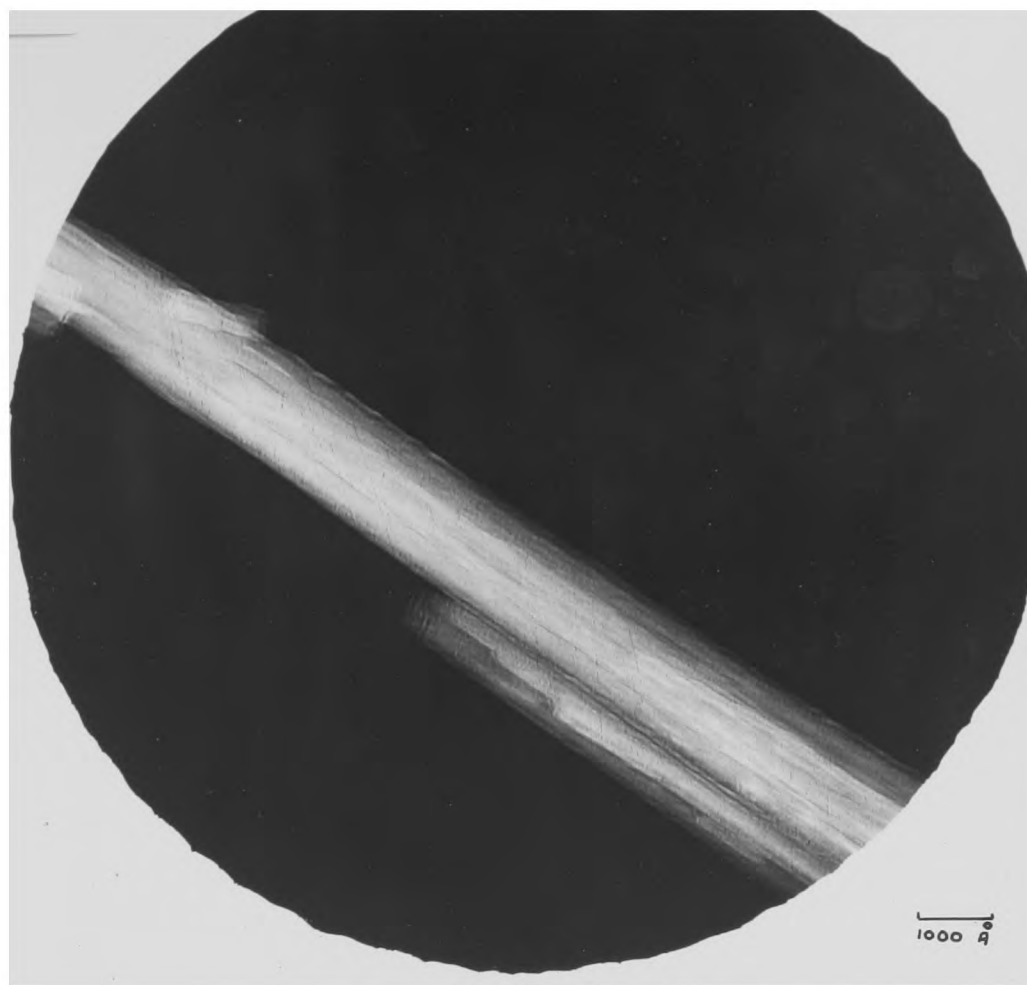


Figure 3.2. Electron diffraction pattern due to para-chrysotile, and matching electron micrograph. Reflections also occur on layer lines appropriate to ortho or clino-chrysotile, (specimen AG 67.761).

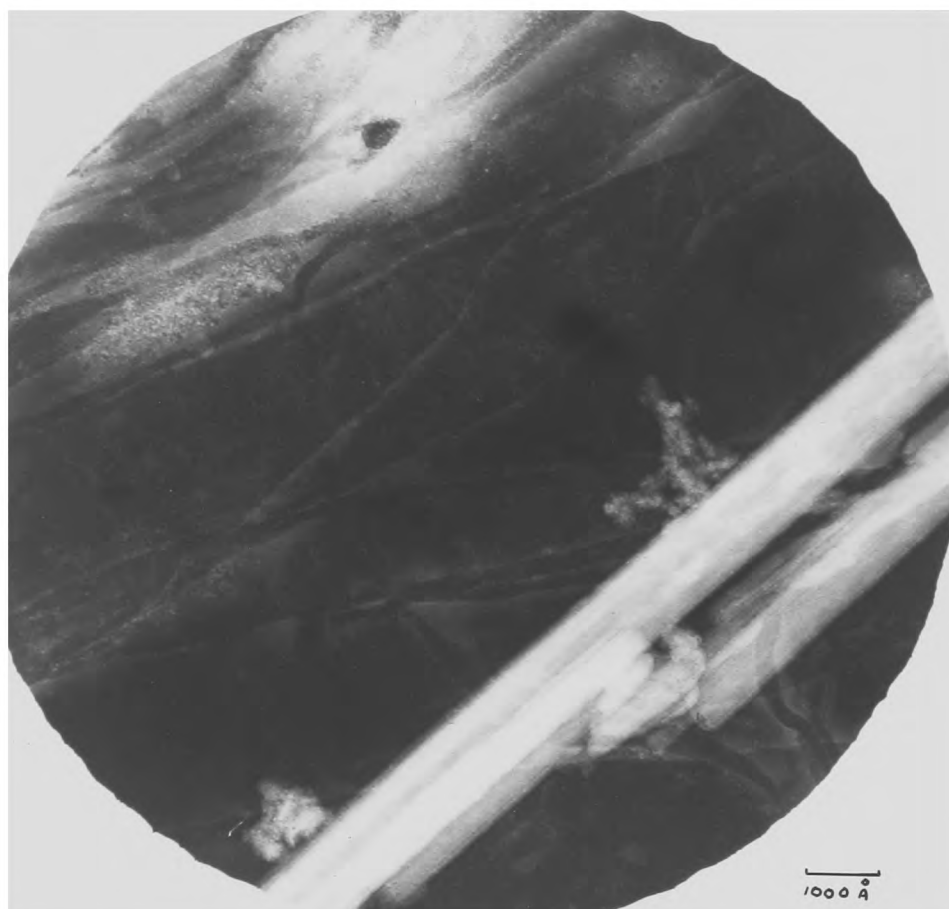


Figure 3.3. Electron diffraction pattern due to para-chrysotile, and matching micrograph. Specimen AG 67.761.

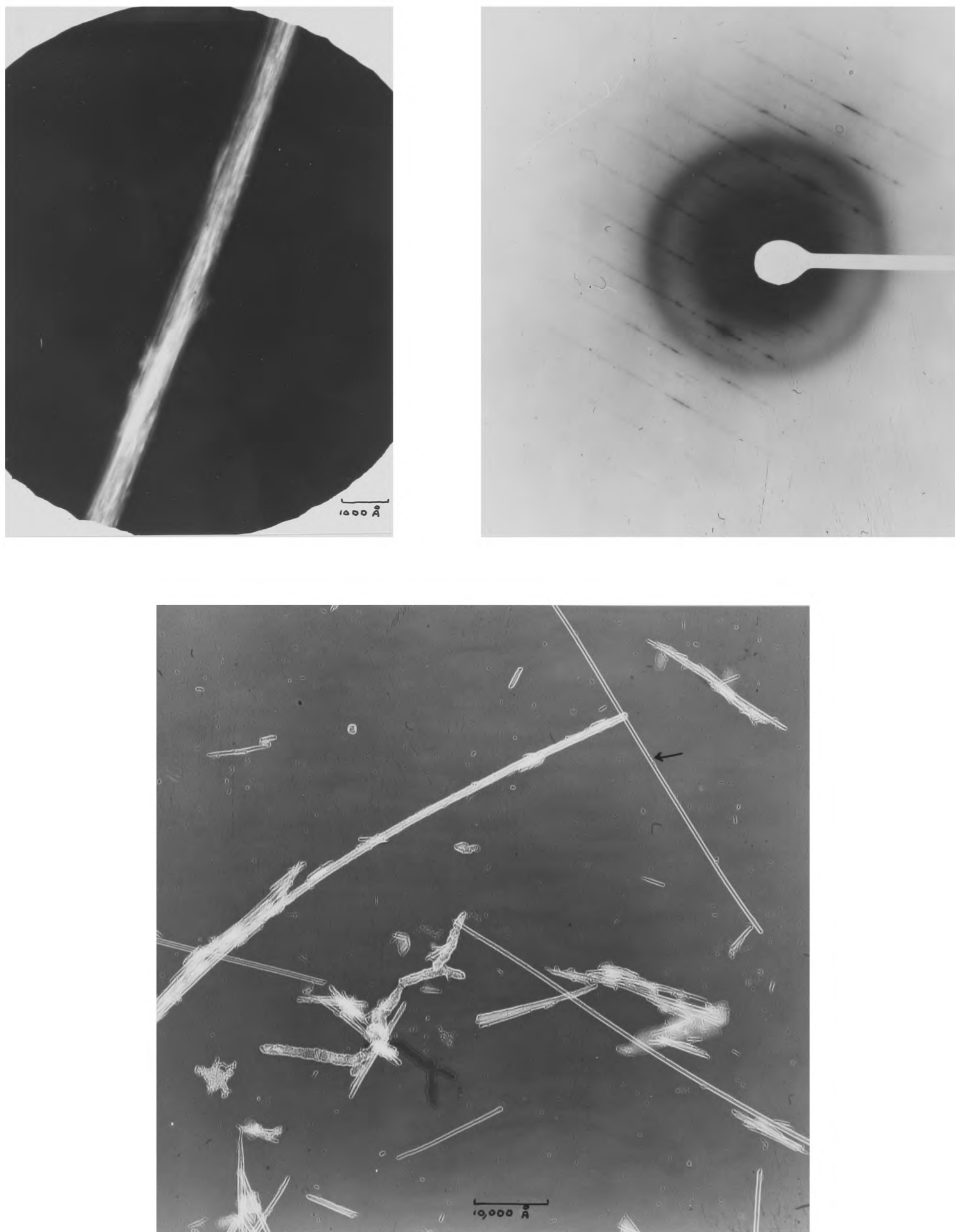


Figure 3.4. Electron diffraction pattern due to para-chrysotile, and matching micrograph; together with a lower magnification electron micrograph of the dispersed fibre sample. The para-chrysotile fibril is arrowed. Specimen AG 67.761.

In addition to the basal reflections several other reflections occur on the zero layer line of para-chrysotile. A somewhat diffuse reflection, which was the only para-chrysotile reflection which could unequivocally be distinguished on this layer line of the x-ray photographs, was indexed as 200. Additionally, there are a few reflections at positions appropriate to $h0l$ type indices. These were not observed in x-ray diffraction, neither are they to be expected from a cylindrical structure curved about the b -axis, (see Tables 3.1 and 3.2 and also section 3.3.2 in which the implications of the electron diffraction data as a whole, are discussed and further comment is made on these and other, unexpected reflections).

On the second layer line a strong meridional reflection, similar to that observed in the x-ray case, was indexed as 020. This reflection has an extended 'tail', which gradually diminishes, with minor oscillations, away from the position $\xi = 0$. Similar meridional reflections (assigned $0k0$ type indices) occur on the other even order layer lines (up to the twelfth*) though the 040, 080 and 0.10.0 reflections are rather weak.

A splitting of the $0k0$ reflections to either side of the meridional position like that observed by Whittaker for the 060 reflection, and advanced by him as evidence for a helical, cylindrical lattice, was not observed.

Additional weak reflections, indexed as $2k0$ type were detected on the fourth and eighth layer lines.

On the sixth layer line which was the highest available on the x-ray photographs, Whittaker observed a series of $06l$ reflections, which provided the evidence that para-chrysotile possesses a two-layer orthorhombic cell ($c = 14.7\text{\AA}$). Similar series of $0kl$ reflections occur on the sixth and twelfth layer lines of the electron diffraction patterns.

* A very weak 0.14.0 reflection can be discerned on the original plate of figure 3.4.

3.2.3 Odd order layer lines

Two diffuse reflections with 'tails', indexable as 110 and 310 and similar in appearance to the $hk0$ reflections of ortho- and clino-chrysotile, can be observed on the first layer line, thus confirming the earlier x-ray observations. Whittaker (1956a) pointed out that these reflections, while generally similar in character to those from cylindrical chrysotile curved about the a -axis, differ in that they occur at ξ values which are integral multiples of b^* but their η values are not integral multiples of a^* , rather than (as in ortho- or clino-chrysotile) having ξ co-ordinates which are integral multiples of a^* and η co-ordinates which are displaced from integral multiples of b^* .

Diffuse reflections, assigned $hk0$ type indices occur on other odd order layer lines up to the ninth. An extremely weak reflection was detected at a level appropriate to the eleventh layer line, on the original plate of figure 3.4; its position could not be measured but seems to be consistent with a 1.11.0 reflection. Whittaker was able to observe $hk0$ reflections on layer lines one and three, but reflections on the fifth and seventh layer lines could not be distinguished from the nearby and considerably stronger, third and fourth layer lines respectively, of clino-chrysotile. Reflections on the ninth layer line were not within the recorded range of the x-ray photographs.

On the third and ninth layer lines unexpected reflections occur at positions suggesting lkl type indices. Reflections of this type were observed by Whittaker (see Table 3.1 and section 3.3.2).

3.5 Interpretation of the electron diffraction patterns of para-chrysotile

3.3.1 Initial considerations and "forbidden" reflections

In common with the fibre diffraction patterns from other varieties of chrysotile the electron diffraction patterns from para-chrysotile exhibit rotational symmetry, and any structural model proposed must account for this feature.

Because of the rarity of para-chrysotile comments concerning its morphology are necessarily few, and usually its intimate association with other material precludes any detailed observations. Yada's (1967, 1971) high resolution investigations have already been mentioned. In the present studies the micrograph of the fibre giving rise to the isolated diffraction pattern of para-chrysotile (figure 3.4) is not remarkable, although it should be noted that this fibre is somewhat coarser than normal silky chrysotile, being $\sim 1000 \text{ \AA}$ in diameter.

If the electron diffraction patterns are indexed on the basis of an orthorhombic cell having the parameters given in Table 3.1, then the following absences may be noted.

<u>Class of Reflection</u>	<u>Absent for</u>
001	$l \neq 2n$
0k1	$k \neq 6n$
hk0 (including the special cases h00 and 0k0)	$h+k \neq 2n$
hkl (including the special case h0l)	$(h+k \neq 2n)$ $(k \neq 3n)$

As has already been mentioned, some of the classes of reflection which are present do not accord well with the notion of a cylindrical structure, curved about the b-axis, in particular those with h0l and hkl type indices.

Because of the close association of the para-chrysotile with other varieties of chrysotile and with brucite the possibility was considered that these unexpected, "forbidden" reflections had been attributed in error to para-chrysotile, and that in fact they had arisen from some other material. The spots concerned cannot, however, be consistently matched against reflections from brucite, and do not occur at positions appropriate to the

layer lines of ortho- or clino-chrysotile. The consistency of their appearance on several diffraction patterns also argues against such an explanation.

Those reflections indexed as 13l type lie (necessarily if they are truly 13l reflections) at the same θ angle as the 20l reflections of ortho-chrysotile (this is apparent in figure 3.3). This feature was noticed at the time when a possible helical model for Povlen-type chrysotile was being investigated, (see chapter two, section 2.3.2). It was found that a similar model to that proposed for Povlen-type chrysotile, but with a helix angle, δ_m of 30° (see figure 2.16), would cause the 20l reflections of ortho-chrysotile to occur on layer three of para-chrysotile, at the required ξ values. Such an explanation for the "forbidden" reflections cannot, however, be valid for reasons exactly similar to those which led to abandonment of the helical model for Povlen-type chrysotile (section 2.3.2.4).

Thus, it seems that the unexpected spots are an essential feature of the fibre diffraction pattern of para-chrysotile. Some slight evidence in favour of this conclusion can be adduced from the diffraction pattern published by Zvyagin (1967)*. Although this pattern is somewhat diffuse, examination of the third layer line (of the para-chrysotile component) shows that the 130 reflection is followed by a stronger intensity maximum and perhaps, by a further weak reflection. The overall profile of this region would thus seem to be similar to that observed in the present studies.

The "forbidden" reflections lie in the tail region of the diffuse 200, 130 and 190 reflections. The reflections from cylindrical para-chrysotile with indices of types h00 and hk0 have been assumed to be analogous in general form to the diffuse 0k0 and hk0 (respectively) reflections of ortho- and clino-chrysotile, but the details of the intensity profiles to be expected

* The diffraction patterns published by Shitov and Zvyagin (1966) are too diffuse to permit detailed observations.

from para-chrysotile have never been investigated. The possibility must be considered that these h0l and hkl type reflections may in fact be merely maxima which are necessary features of the tails of the diffuse reflections of para-chrysotile. Therefore the profiles of some of the diffuse reflections which would arise from cylindrical para-chrysotile were computed.

3.3.2 Computation of the profiles of some diffuse reflections

The method of calculation adopted in this instance was essentially the same as that described in chapter two, being derived from the treatment by Whittaker (1956b, 1957), who calculated the intensity profiles of some of the diffuse reflections from ortho- and clino-chrysotile. Modification of the expressions given was required to take account of the different axis of curvature, and for ease of comparison with the expressions derived by Whittaker the axial convention used by that author was maintained*. The meanings of the symbols to be used will not be repeated here as they have already been given in section 2.3.1 of chapter two.

An expression giving the intensity of radiation scattered by a cylindrical structure appropriate to ortho- and clino-chrysotile was given by Whittaker (1957) - equation 2.1 in this paper. In a form modified to render it applicable to para-chrysotile, this expression becomes -

$$I(\xi, k) = 2 \frac{Q^2}{R^2} \sum_m \sum_L P_m^2 \left\{ \left| \sum_j f_j \exp\left(2\pi i k \frac{y_j}{b}\right) \cos\left(2\pi \frac{Lz_j}{c}\right) J_{LP_m}\left(P_m \frac{c_{m,j}}{c} \cdot l\right) \right|^2 \right. \\ \left. + \left| \sum_j f_j \exp\left(2\pi i k \frac{y_j}{b}\right) \sin\left(2\pi \frac{Lz_j}{c}\right) J_{LP_m}\left(P_m \frac{c_{m,j}}{c} \cdot l\right) \right|^2 \right\}$$

Equation 3.1

* i.e. the 200 reflection will be referred to as 002, 110 as 011 and 130 as 031 to accord with the interchange of the a and c crystallographic axes.

This expression formed the basis of the calculations, which were carried out using a computer program, PARA (Appendix A). As in the calculations described in chapter two the atomic co-ordinates used were those of Whittaker (1957; reproduced as Table 2.4) and again, for the sake of simplicity and direct comparability with the earlier work the scattering factors used were the empirical temperature-corrected values of Bragg and West (1928, Table VII).

The equivalent positions in the appropriate two-dimensional space group are as follows (Whittaker (1957), p.150) -

$$\begin{aligned} \text{Fourfold: } & y, z \quad ; \quad \bar{y}, z \\ & \frac{1}{2}+y, \frac{1}{2}+z \quad ; \quad \frac{1}{2}-y, \frac{1}{2}+z \\ \text{Twofold: } & 0, z \quad ; \quad \frac{1}{2}, \frac{1}{2}+z \end{aligned}$$

Substitution of these values led to some simplification of the diffraction formula for ortho-chrysotile (section 2.3.1), but the same disappearance of certain terms does not occur when the values are substituted into the para-chrysotile formula.

Equation 3.1 can conveniently be expressed as -

$$I(\xi, \kappa) = 2 \frac{Q^2}{R^2} \sum_m \sum_L P_m^2 \{ |A|^2 + |B|^2 \}$$

$$A = \sum_j f_j \exp \left(2\pi i \kappa \cdot \frac{y_j}{b} \right) \cos \left(2\pi \frac{Lz_j}{c} \right) J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right)$$

$$B = \sum_j f_j \exp \left(2\pi i \kappa \cdot \frac{y_j}{b} \right) \sin \left(2\pi \frac{Lz_j}{c} \right) J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right)$$

When the co-ordinates of the equivalent positions have been inserted into these expressions they can be written as -

$$\begin{aligned} A &= \sum_j u_j f_j \cos 2\pi Lz_j \cdot J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right) \\ B &= \sum_j u_j f_j \sin 2\pi Lz_j \cdot J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right) \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \end{array} \right\} \text{Equations 3.2}$$

where $u_j = 2$

$$\begin{aligned} \text{and } A &= \sum_j u_j f_j \cos 2\pi Lz_j \cdot \cos 2\pi \kappa y_j \cdot J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right) \\ B &= \sum_j u_j f_j \sin 2\pi Lz_j \cdot \cos 2\pi \kappa y_j \cdot J_{LP_m} \left(P_m \cdot \frac{c_{m,j}}{c} \right) \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \end{array} \right\} \text{Equations 3.3}$$

where $u_j = 4$

appropriate to the twofold and fourfold atoms respectively.

The multiplicity values, u are therefore as follows -

$$u = 2 \text{ for } O_1, OH_1, Mg_1 \text{ and } OH_2.$$

$$u = 4 \text{ for } Si, O_3, Mg_2 \text{ and } OH_3.$$

$$u_{02} = 4 \text{ when } L = 2n$$

$$0 \text{ when } L = 2n + 1.$$

A computer program "PARA" was written to perform the calculations, it is described in Appendix A.

The intensity data derived from the calculations were weighted according to the same scheme as that discussed in chapter two, this facility was written into the program. The use of such statistical weights while valid in the case of x-ray diffraction of a fibre bundle containing many individual fibrils, is not applicable to the case of electron diffraction when we are observing the diffraction effects from a very few (or single) fibrils. Thus, while the fibrils selected in a number of instances may be of various diameters, in a particular diffraction experiment the inner and outer diameters are (ideally) unique or nearly so. Each layer present (in a fibril with those particular inner and outer diameters) should therefore be given unit weight.

The unexpected diffraction effects noted in the present studies might then be a special feature deriving from the observation of single fibrils in the electron microscope. Reflection profiles to be expected from various combinations of inner and outer diameters were therefore computed.

Intensity profiles were calculated for three reflections - 011, 002 and 031. The profile of 011 was calculated even though no "forbidden" reflections occur in the tail region of this reflection. This was done in order to provide a control on the fibril diameters adopted, such that the 011 profile resulting from the application of a particular set of weights should not show any unusual features.

Representative computed profiles of the 002, 011 and 031 reflections are presented in figures 3.6, 3.7 and 3.8 respectively, for various fibril size distributions (applicable to x-ray diffraction), and "unit-weight" distributions (applicable to electron diffraction). These may be compared with the observed profiles of these reflections, shown in figure 3.5.

The calculated profile of the 011 reflection of para-chrysotile is similar to that of the corresponding reflection from ortho- or clino-chrysotile, except that there is no evidence of a subsidiary maximum at $l \approx 2$, which was noted in the calculated profiles of the latter (at $k \approx 2$). The variation of fibre parameters has little effect on the profile of this reflection.

Both the 002 and the 031 calculated reflection profiles are markedly more irregular than the 011 profile. A feature of the 002 profile is the appearance of a series of regularly spaced, sharp, subsidiary maxima at $l \approx 2.75, 3.25, 3.75$. The profile of this reflection can be seen to be sensitive to changes in fibre parameters. The profile of the 031 reflection is characterised by a broad 'hump', the intensity and 'smoothness' of which vary with the fibre parameters - the thinner-walled "unit-weight" distributions giving rise to less intense, more irregular profiles. Superimposed upon this hump are a sharp minimum at $l \approx 2.5$ and a sharp maximum in the region $l = 2.85$ to 2.9 .

Thus, while these profiles of the diffuse reflections to be expected from para-chrysotile are generally analogous to the diffuse reflections from ortho- or clino-chrysotile, they do differ in detail. But the computed profiles do not match the observed diffraction effects, so that we cannot explain the "forbidden" reflections as being essential features of the diffuse reflections of para-chrysotile.

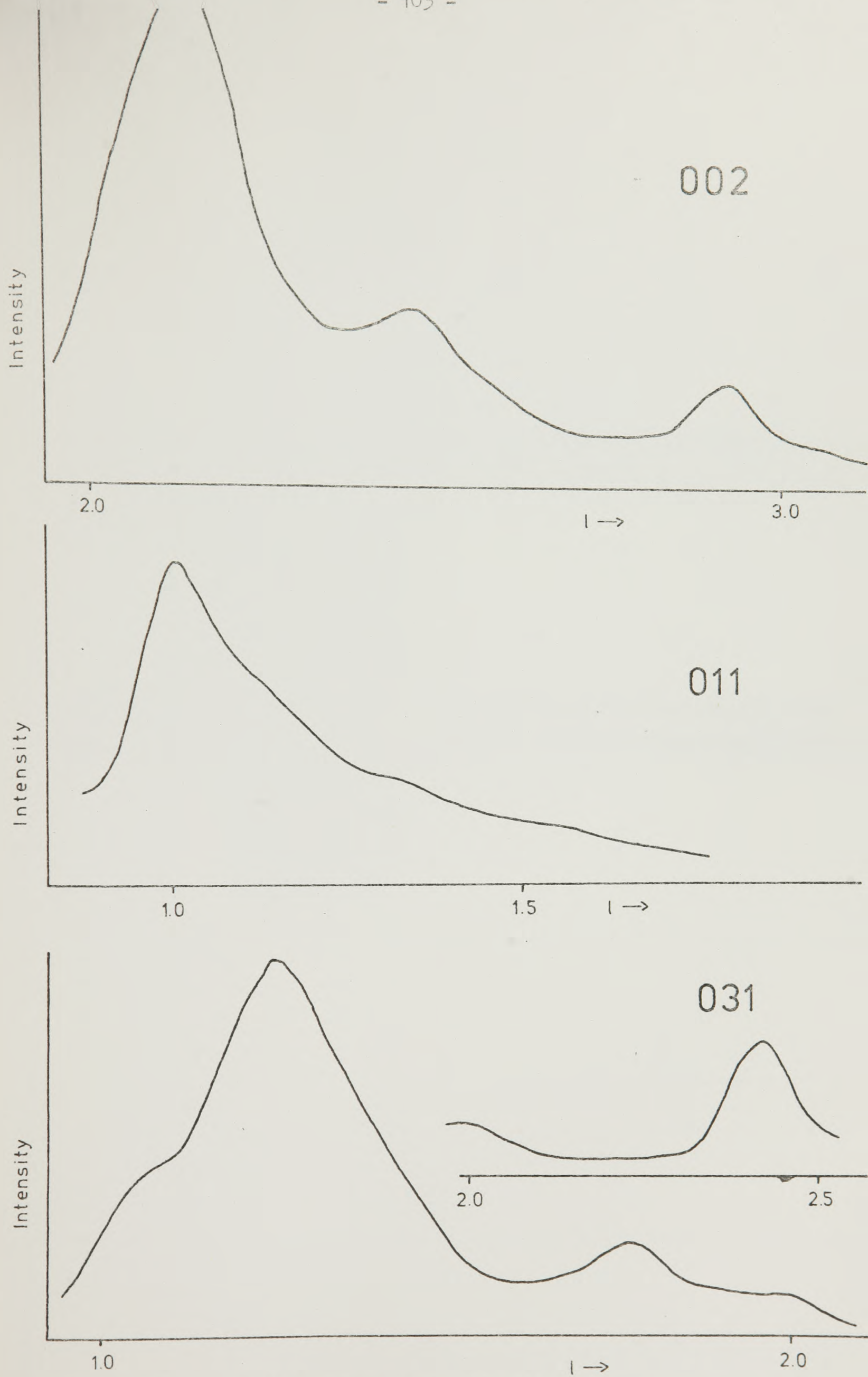


Figure 3.5. Observed profiles of the 002, 011 and 031 reflections of para-chrysotile, in electron diffraction; specimen AG 67.761.

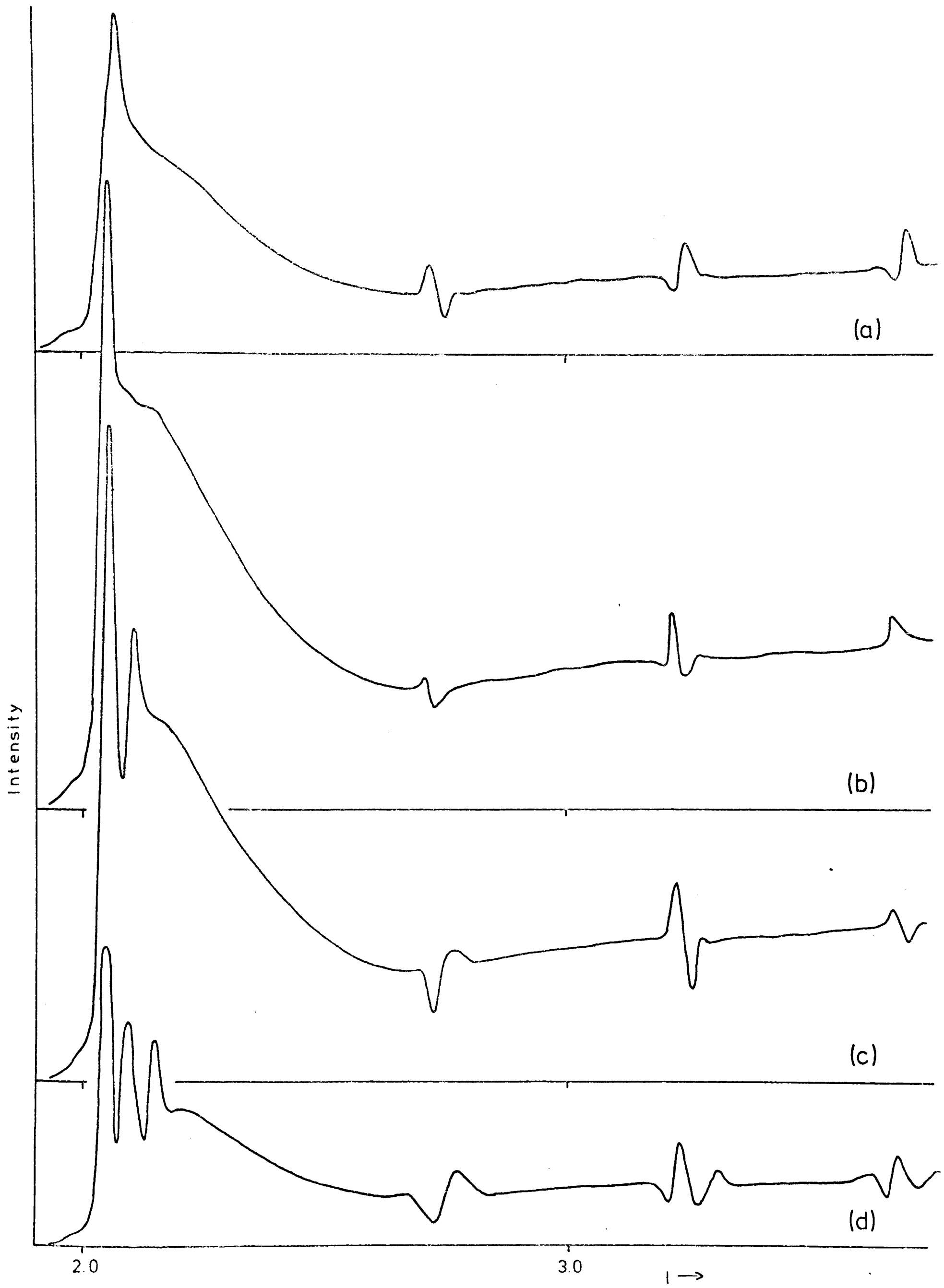
Figure 3.6

Representative weighted profiles calculated for the 002 reflection of para-chrysotile. Profiles (a) to (d) are appropriate to x-ray diffraction of fibre bundles :

- (a) $m_o = 12, t = 10$
- (b) $m_o = 20, t = 25$
- (c) $m_o = 25, t = 100$
- (d) $m_o = 25, t = 1000$

Profiles (e) to (h) are appropriate to electron diffraction of individual fibrils, with m_1 and m_2 as the innermost and outermost layers respectively :

- (e) $m_1 = 3, m_2 = 40$
- (f) $m_1 = 3, m_2 = 30$
- (g) $m_1 = 25, m_2 = 35$
- (h) $m_1 = 3, m_2 = 21$



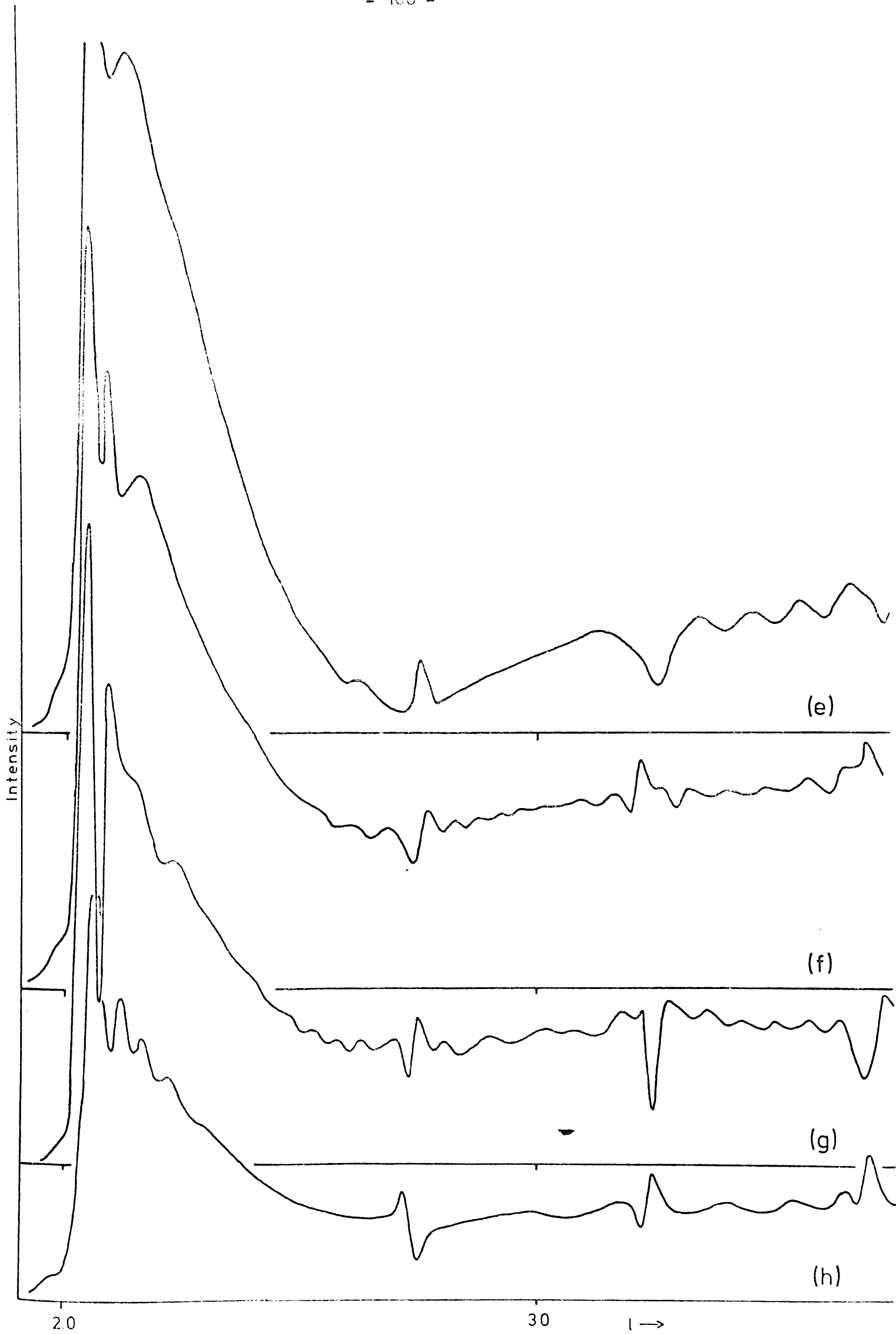


Figure 3.7

Representative weighted profiles calculated for the 011 reflection of para-chrysotile. Profiles (a) and (b) are appropriate to x-ray diffraction of fibre bundles :

$$(a) m_o = 12, t=10$$

$$(b) m_o = 20, t=25$$

Profiles (c), (d) and (e) are appropriate to electron diffraction of individual fibrils, with m_1 and m_2 as the innermost and outermost layers respectively :

$$(c) m_1 = 3, m_2 = 40$$

$$(d) m_1 = 3, m_2 = 30$$

$$(e) m_1 = 3, m_2 = 21$$

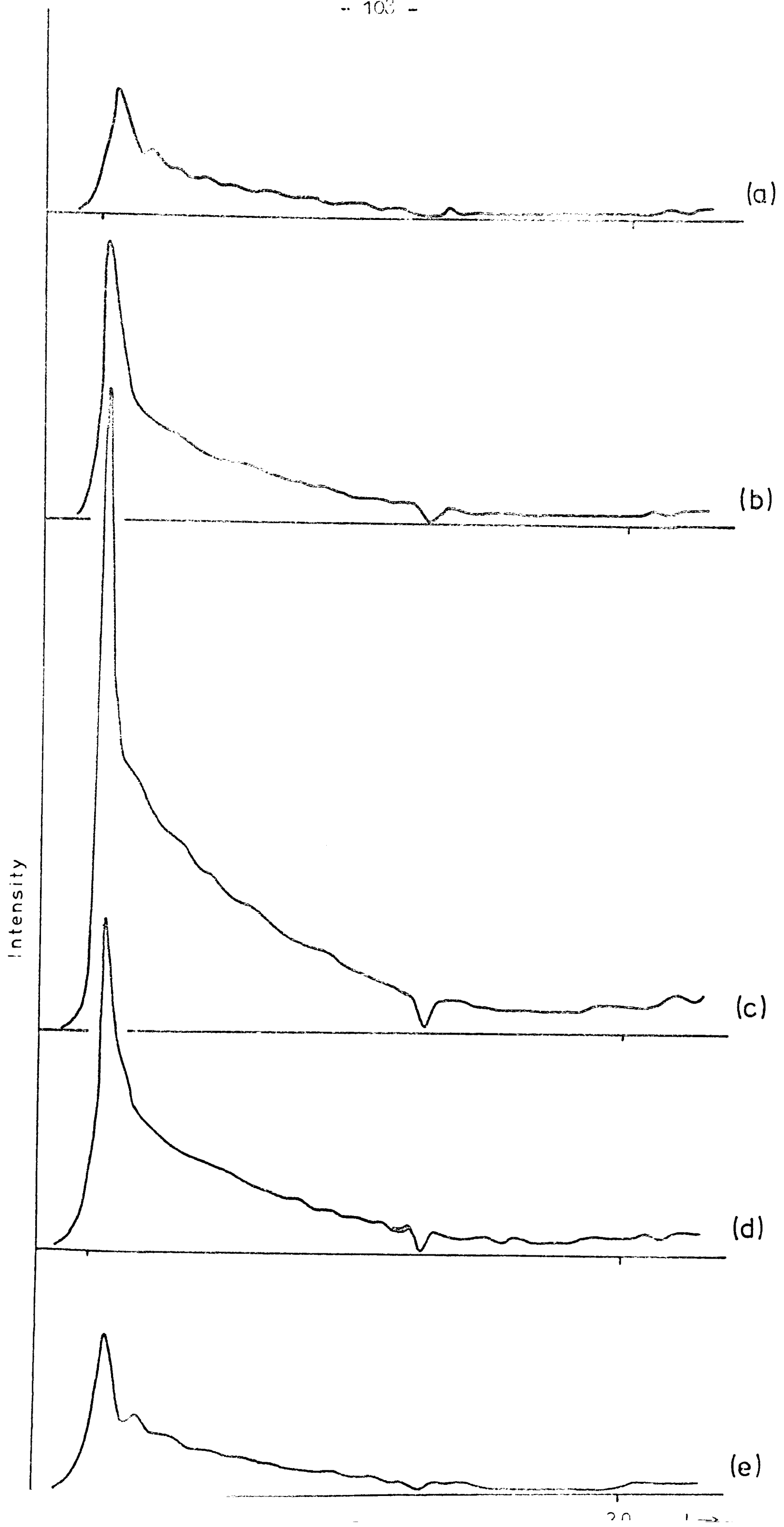


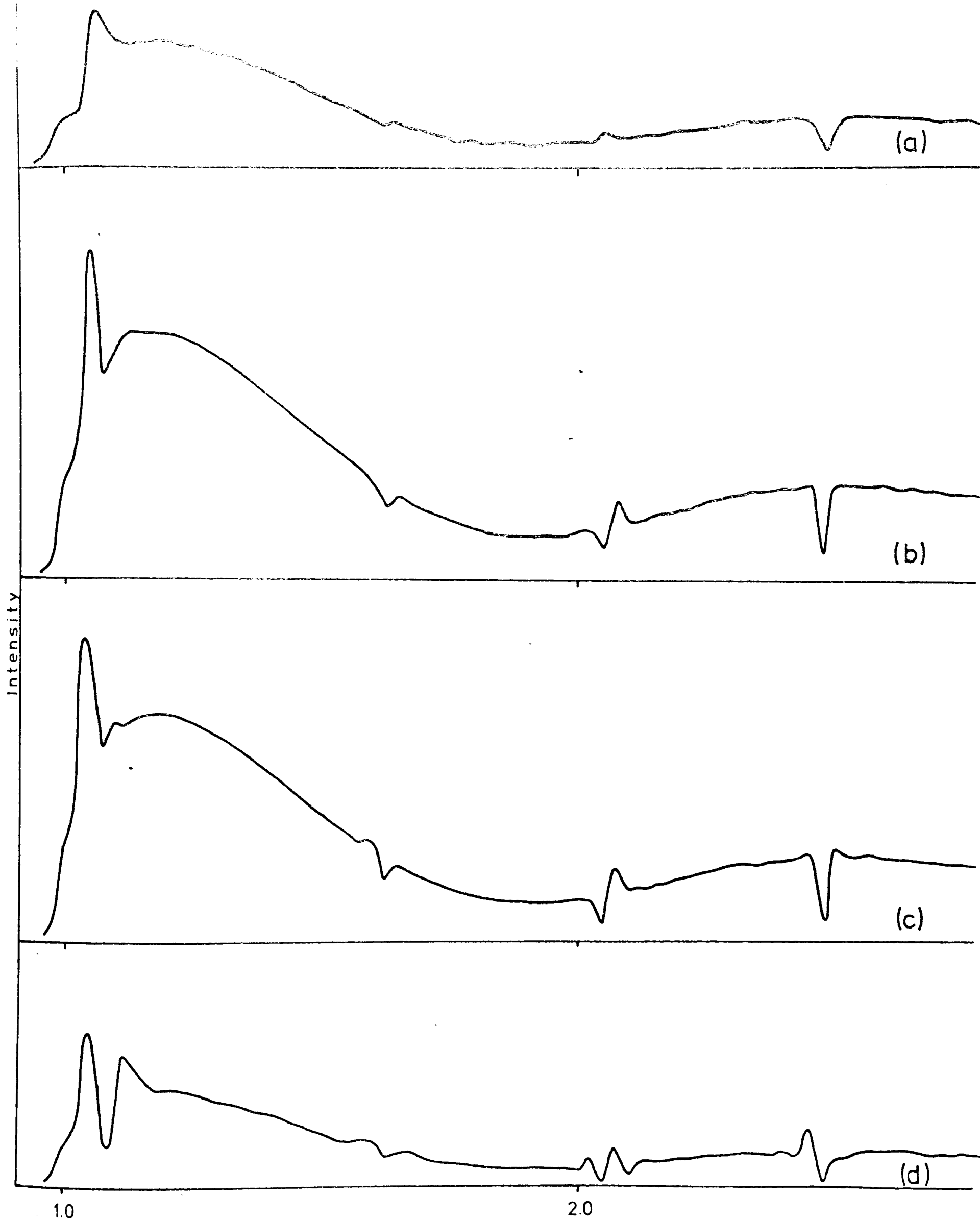
Figure 3.8

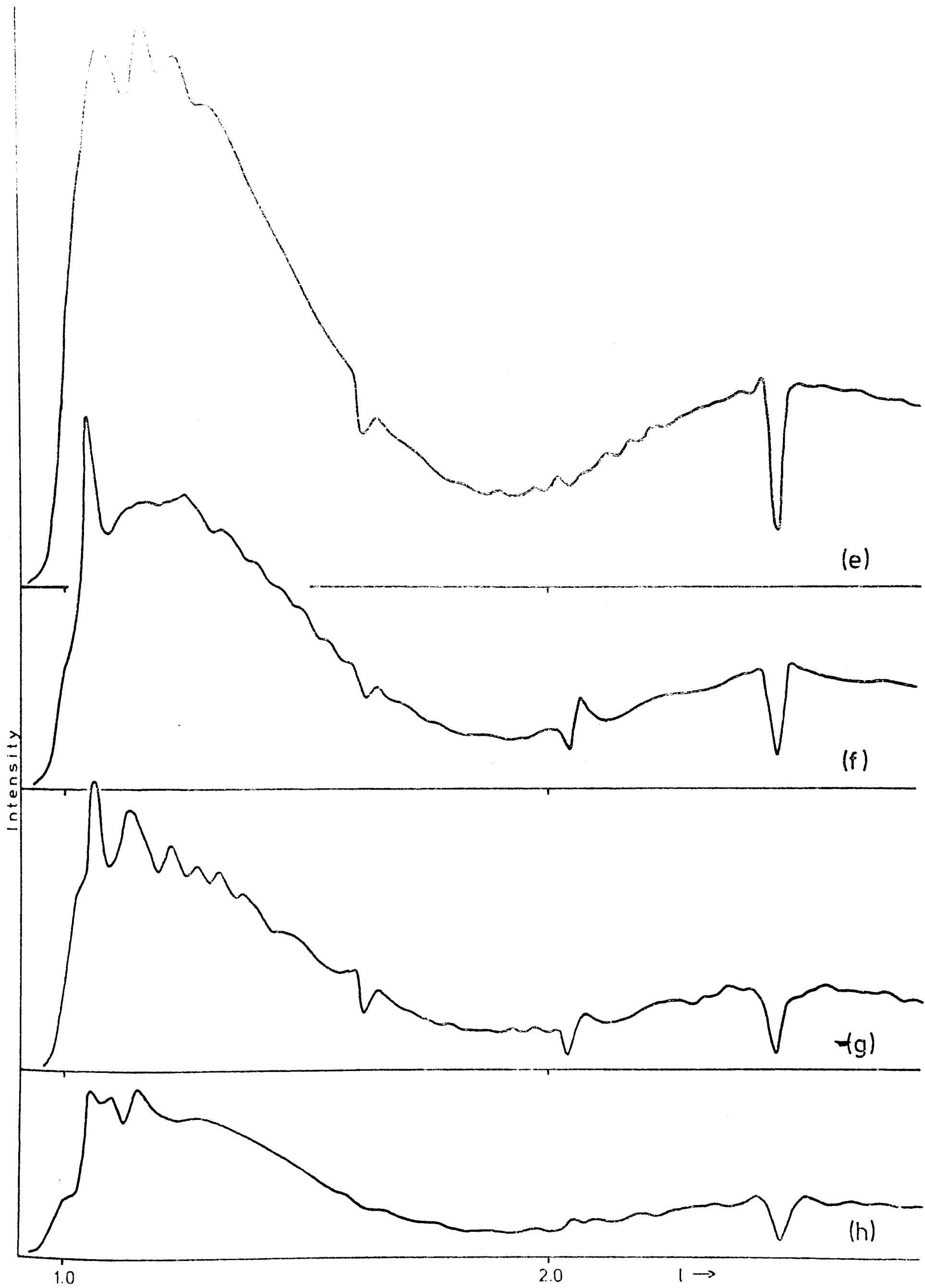
Representative weighted profiles calculated for the 031 reflection of para-chrysotile. Profiles (a) to (d) are appropriate to x-ray diffraction of fibre bundles :

- (a) $m_o = 12, t = 10$
- (b) $m_o = 20, t = 25$
- (c) $m_o = 25, t = 100$
- (d) $m_o = 25, t = 1000$

Profiles (e) to (h) are appropriate to electron diffraction of individual fibrils, with m_1 and m_2 as the innermost and outermost layers respectively :

- (e) $m_1 = 3, m_2 = 40$
- (f) $m_1 = 3, m_2 = 30$
- (g) $m_1 = 25, m_2 = 35$
- (h) $m_1 = 3, m_2 = 21$





3.5.3 A polygonal model ?

If we are to explain all of the reflections attributed to para-chrysotile in the electron diffraction patterns, then the acceptance of some indices of types which demand at least a degree of three dimensional order, seems to be inevitable. This raises a conflict, similar to that encountered when attempts were made to index the fibre diffraction patterns from Povlen-type chrysotile (chapter two). In the outcome it appears that the polygonal model proposed for that variety may also have some application to para-chrysotile.

The marked rarity of para-chrysotile as compared with both clino- and ortho-chrysotile indicates that some feature operates against the curvature of chrysotile layers about their b-axes. It is suggested that this might be related to some limitation to the stacking of layers curved about this axis, such that complete azimuthal inter-layer disorder, in the a-axis direction, inherent in the stacking of layers in such a cylindrical structure, is not easily achieved.

Therefore it is proposed that chrysotile layers are rarely (if ever) curved about their b-axes and that para-chrysotile, like Povlen-type chrysotile, possesses a polygonal structure. The usual observation of para-chrysotile in association with other varieties of chrysotile, even when apparently single fibrils have been examined, may reflect a mode of growth in which flat, polygonally arranged layers, oriented with their b-axes parallel to the fibre axis, are deposited on a pre-existing core of normal, cylindrical chrysotile. The growth of layers in this orientation might be promoted by the intergrowth of chrysotile with brucite (or with one of the structurally, closely related minerals, such as pyroaurite - see chapter seven).

If the structure of para-chrysotile can be described in terms of such a polygonal model, we would expect a 'lumpiness' in the diffuse reflections, similar to that observed in Povlen-type chrysotile (section 2.3.3.2). This effect is not apparent in the hko reflections but this may be due in part to their relative weakness. The 020 reflection on the other hand (which is of considerably greater intensity) clearly shows sharp oscillations of intensity within its 'tail'.

The relationship between successive chrysotile layers in a polygonal structure is likely to be different to that in a cylindrical structure, as was discussed for the case of Povlen-type chrysotile in chapter two. Whittaker (1956a) pointed out that if the layers were arranged cylindrically in para-chrysotile (with complete interlayer disorder in the a-axis direction), then the hydroxyl groups would behave "as corrugations having troughs at $y = (2n+1)/12$, i.e. at intervals of $b/6$ ". Thus, it would be reasonable to assume that random interlayer shifts of $\pm nb/6$ might occur, which would explain the absence of $Ok1$ reflections except when $k = 6n$.

The present results appear to confirm the absence of $Ok1$ reflections for which $k \neq 6n$, such reflections occurring only on the 0th, 6th and 12th layer lines. However, the acceptance of some hkl type indices and their implications regarding ordered stacking of layers, requires a reconsideration of the interlayer shifts to be expected for the model proposed.

Reference to figure 1.1 indicates that interlayer shifts of $\pm nb/6$ may still occur, but that when $n = \text{odd}$ they must be accompanied by a shift of $\pm ma/2$ ($m = \text{odd}$). A shift such as $b/6 + a/2$, however, produces a result which is equivalent to a shift of $2b/3$. Thus, it seems that random interlayer shifts of $\pm nb/3$ may occur, and explain the absence of all

hkl reflections for which $k \neq 3n$. A further condition, imposed by centring of the lattice is that hkl reflections are absent when $h + k \neq 2n$. Therefore $Ok1$ reflections for which $k = \text{odd}$ - in particular 031 , 091 - will not occur, leading to the apparent restriction of $Ok1$ reflections to layer lines for which $k = 6n$.

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CHAPTER FOUR

Some observations on fibrous brucite

4.1 Introduction

In this chapter are presented the results of a limited number of observations on fibrous brucite samples (fibrous brucite was termed nemalite by Nuttall, 1821; see Palache, Berman and Frondel, 1944), taken from veins cutting serpentinite specimens from Jeffrey mine, Quebec. After a brief account of the findings of the present studies, these results, together with other published information are taken as the basis of a discussion of the nature of the association of brucite with chrysotile. Some points of wider relevance to considerations of the process of serpentinisation, arising from considerations of the occurrence of brucite in serpentinites, are discussed in chapter six.

Brucite associated with serpentinites is commonly iron bearing and may turn brown on exposure. The proportion of the $\text{Fe}(\text{OH})_2$ end member present (the "ferruginosity" - Shteynberg and Chashchukhin, 1969) in a brucite sample can be simply determined using the x-ray diffractometer technique. Mumpton and Thompson (1966) assumed that there is a linear variation of the basal spacing of brucite (i.e. d_{0001}) with substitution of Fe^{2+} for Mg in brucite, between the values for the two end members $\text{Mg}(\text{OH})_2$ ($d_{0001} = 4.77 \text{ \AA}$: Anon, 1956), and $\text{Fe}(\text{OH})_2$ ($d_{0001} = 4.597 \text{ \AA}$: Bernal, Dasgupta and Mackay, 1959).

On the basis of this assumption they determined the ferruginosities of brucite samples from the New Idria serpentinite, California. Their estimates by this method showed good agreement with the results of chemical analysis and microprobe determinations. The method was again used successfully by Page (1967). Normal chemical methods and even microprobe investigation of the composition of brucite in serpentinites frequently suffer from problems similar to those encountered when attempts are made to

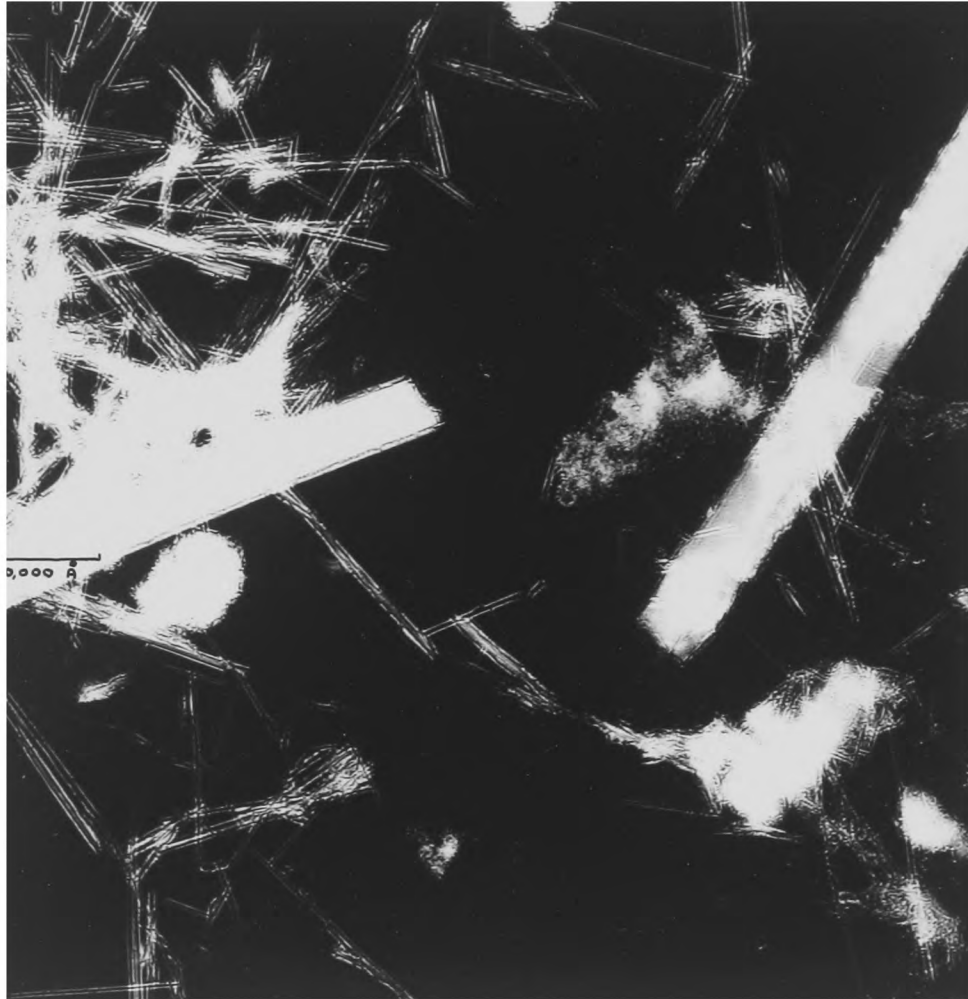


Figure 4.1. Low magnification electron micrograph of dispersed material from sample AG 67.761, showing the distinctive morphologies of brucite (broad laths) and chrysotile.

analyse the serpentine minerals - namely the extreme fineness of scale of some of the textural intergrowths of the minerals, with the resultant uncertainty as to what in fact is being analysed. The approach of Mumpton and Thompson (1966) therefore provides a very useful semi-quantitative method for estimating the degree of iron enrichment of brucites associated with serpentinites.

The ferruginosities of the vein brucite samples investigated in the present studies were determined using this method and found to be relatively low (generally less than 5% $\text{Fe}(\text{OH})_2$, see Table 7.1 and chapter seven for further discussion of the chemistry of brucite in serpentinites).

The nature of fibrous brucite and its intergrowth with chrysotile was investigated using x-ray and electron diffraction methods. Most of the fibres examined gave x-ray rotation photographs with well developed layer lines indicating a fibre repeat of $\sim 3.1 \text{ \AA}$. Thus, these photographs suggest well oriented brucite with an a-axis ($a = 3.14 \text{ \AA}$, Deer et al, 1962) lying parallel to the fibre axis. In some photographs weak reflections were observed on layer lines indicating a fibre repeat of $\sim 5.4 \text{ \AA}$. These reflections are derived from brucite with an orthohexagonal b-axis ($b = a \sqrt{3} \approx 5.4 \text{ \AA}$) lying parallel to the fibre axis. Reflections due to chrysotile in parallel orientation with brucite (particularly the series of basal reflections on the zero layer line) were detected on several of the photographs. X-ray oscillation photographs indicated that the fibres were in fact aggregates, with several brucite crystallites all arranged with an a-axis parallel to the fibre axis, but in random orientation about that axis.

In the electron microscope brucite is seen to possess a lath-like morphology, often displaying a sharp (cleavage) outline; it is thus easily distinguished from associated chrysotile fibrils (see figure 4.1).

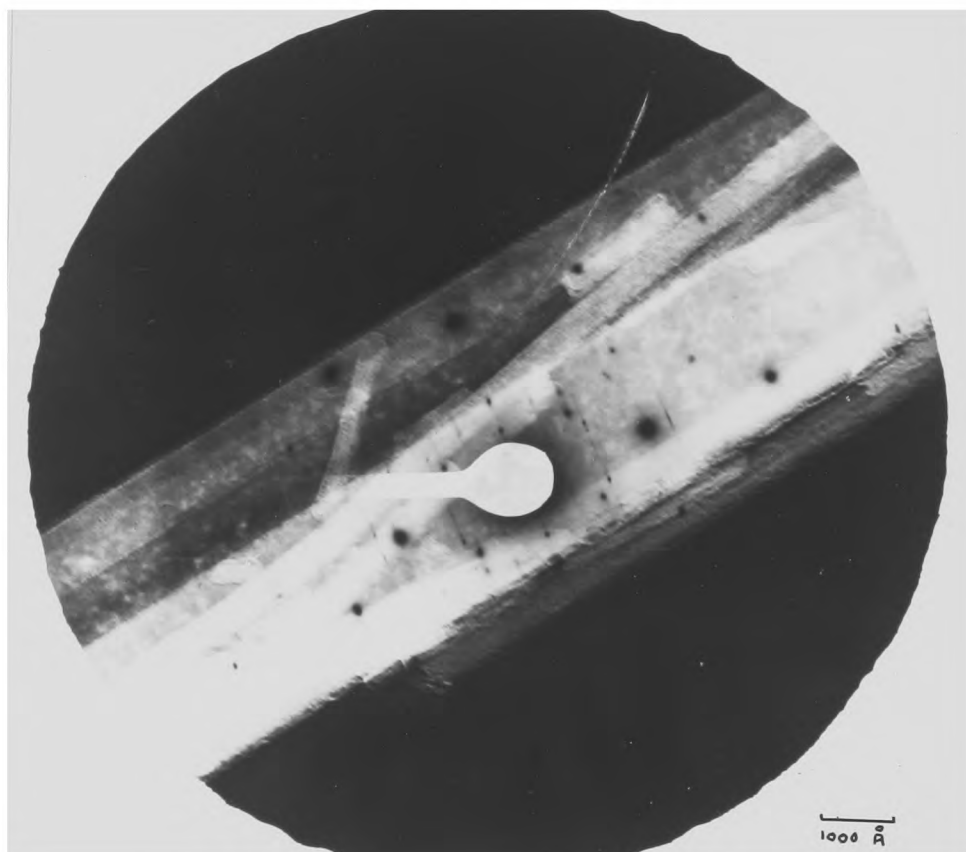
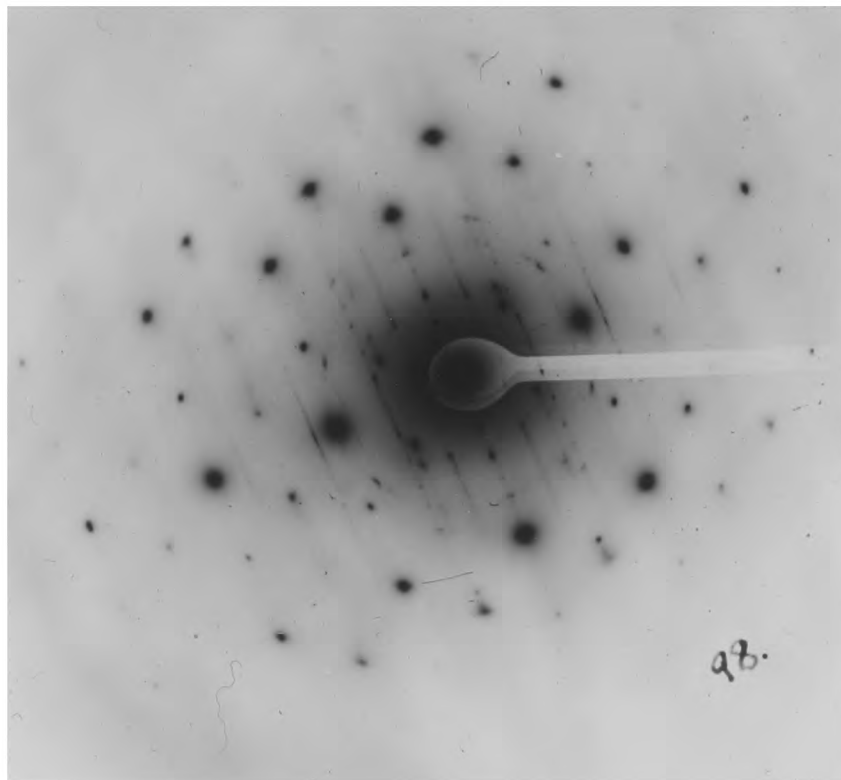


Figure 4.2. Electron micrograph of a composite lath and its diffraction pattern, which exhibits reflections due to brucite, clino-chrysotile and para-chrysotile. Specimen AG 67.761.

During examination of one sample (AG 67-761) in the electron microscope, diffraction patterns were observed which indicated brucite (with an a-axis parallel to the fibre axis) in parallel growth with para-chrysotile, as well as with clino-chrysotile (see figure 4.2). No examples were seen in electron diffraction of brucite oriented with a b-axis parallel to the fibre axis. In contrast to the chrysotile components of the electron diffraction patterns, the pattern due to brucite does not exhibit evidence of rotational symmetry about the fibre axis, but can be interpreted as a section through the reciprocal lattice in the $a^* c^*$ plane. This is somewhat surprising as it would be expected that the brucite laths would lie with their thin direction parallel to the electron beam, that is with the c^* axis parallel to the beam. This would give rise to a diffraction pattern indicating an $a^* b^*$ (orthohexagonal) section through the reciprocal lattice, such as that observed by Liebling and Langer (1972). The evidence of rotational disorder about the fibre axis, adduced from x-ray photographs lends some further weight to the observation of brucite in this orientation.

Optical examination of dispersed fibre samples using a petrological microscope served to confirm the published accounts of the optical characteristics of nemalite (see below, 4.2.3).

4.2 Review and Discussion

4.2.1 Structure and Chemistry

Before considering the textural characteristics of nemalite and its intergrowth with chrysotile, in the light of the results of diffraction experiments, the general structural features of brucite will be summarised, together with a brief account of its chemical features.

The layered structure of brucite, $\text{Mg}(\text{OH})_2$ was determined by Aminoff in 1919 (Deer et al, 1962) who demonstrated that two sheets of hydroxyls, each in hexagonal close packing and between them a plane of octahedrally co-ordinated magnesium atoms constitute each layer. The brucite structure possesses trigonal symmetry with cell constants $a = 3.14 \text{ \AA}$ and $c = 4.76 \text{ \AA}$ (Deer et al, 1962).

Brindley and Ogilvie (1952) re-examined the brucite structure in an x-ray study, using fine single crystals of tubular habit, from Woods mine, Texas (Pa.). Their study was undertaken in order to investigate the possibility that stacking faults occurred in the sequence of layers, as is commonly the case in silicate minerals with layered structures. No evidence of such stacking faults was apparent, but from the investigation they obtained evidence that the crystals studied, possessed a texture in which there was apparently a misorientation (by a few degrees) of the c-axes of individual crystallites, relative to the morphological c-axis - see figure 4.3 (after Brindley and Ogilvie). Brindley and Ogilvie suggested that this texture might arise from a bending of the structure about a-axis directions, due in turn to sets of edge dislocations.

Deer et al (1962) have pointed out that although nemalite is often reported to be iron rich, it frequently appears so only by virtue of fine grained inclusions of magnetite. This is clearly suggested by the work of Donnay (1944), which is discussed below (section 4.2.3). During the present studies intergrowths of brucite with magnetite have been observed and are discussed briefly in chapter five.

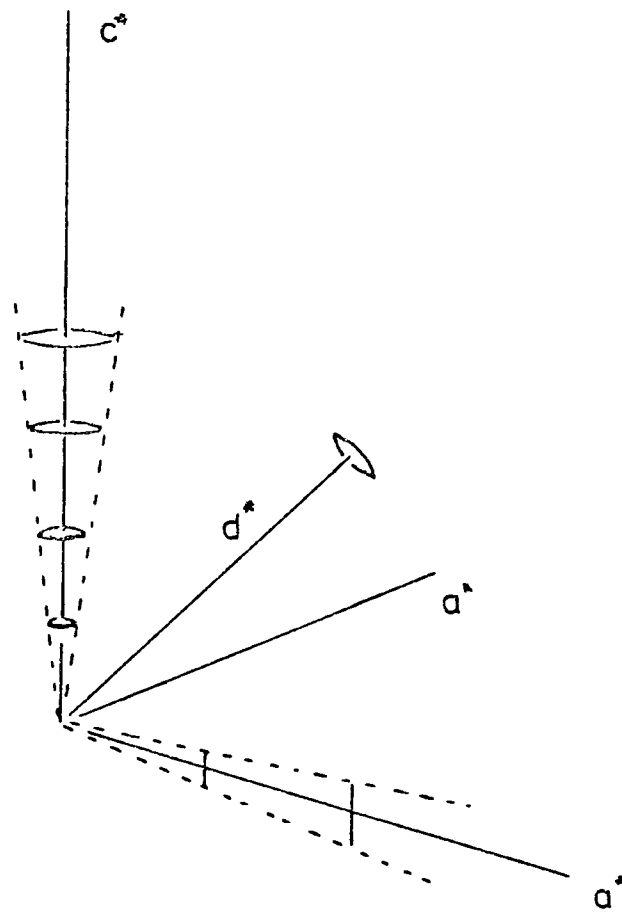


Figure 4.3. Diagram to illustrate the effect on reciprocal lattice points of small rotations of the lattice about a-axis directions, (Brindley and Gilvie 1952, figure 1).

Berman (1932) gave a chemical analysis of fibrous brucite providing values for both ferrous and ferric iron. Donnay (1944) recalculated this analysis (assuming that all the ferric iron and sufficient ferrous iron, represented inclusions of magnetite) to give a formula for the iron-brucite: $(\text{Mg}_{0.925} \text{Fe}_{0.075}) (\text{OH})_2$. The material studied by Garride (1936) on the other hand was reported to contain only about 1% total iron, by 'spectral analysis'. Page (1967) reported brucite-associated with serpentinites, but not necessarily fibrous - with up to 50% $\text{Fe}(\text{OH})_2$, from Burro Mountain, California, while Shteynberg and Chashchukhin (1969) gave values in the range 6.5 to 20.7% $\text{Fe}(\text{OH})_2$ for brucite occurring in several Russian serpentinites.

It seems then that the iron content of brucite is variable and can attain high values but that the fibrous variety of nemalite is not necessarily particularly iron rich.

4.2.2 The texture of fibrous brucite and its intergrowth with chrysotile

Prior to consideration of the details of the orientation of brucite in fibrous specimens it is necessary to clarify the nomenclature of zone axes in the hexagonal system, both to clarify discussion of previous work and also to make clear the nomenclature used in this thesis.

References to this topic in the standard texts (e.g. Henry, Lipson and Wooster, 1960; Palache, Berman and Frondel, 1944; Phillips, 1963) are in general rather brief. In the International Tables (Kasper and Lonsdale, 1959), however, zone axes in the hexagonal system are referred to by symbols of the form $(uv0w)$. In the footnote to page 115 the authors (Donnay and Donnay, 1959) state that this is not a Weber* four-figure symbol but is derived by reference to only two of the three horizontal crystallographic axes. In this case it would seem to be unnecessarily misleading to represent the third index, even by a zero, which implies that it has a significant value.

* Zeit, Krist. 57, 200 (1922).

Similarly if a point were to be used in place of the third index this would suggest, by analogy with face indices of the form (hk.l) that a meaningful index had been omitted but that it need not be specified because it could be derived from the first two indices.

The nomenclature used here for zone symbols referred to only two of the three horizontal axes is therefore of the form: $\angle \bar{u}v\bar{w}$; Weber four figure symbols will be written in the form $\angle \bar{U}VJ\bar{W}$ and symbols of the form $\angle \bar{u}vO\bar{w}$ will not be used. When reference is made to three or four figure symbols of undefined type given in the literature, these will be enclosed in quotation marks, viz " $\angle \bar{u}v\bar{w}$ ", " $\angle \bar{u}vJ\bar{w}$ ".

Rules are given by Donnay and Donnay for the derivation of the Weber symbol $\angle \bar{U}VJ\bar{W}$ from the three figure symbol, $\angle \bar{u}v\bar{w}$ as follows:

$$U = u - (u+v) / 3 \quad (1)$$

$$V = v - (u+v) / 3 \quad (2)$$

$$J = - (U+V) \quad (3)$$

It is explicitly stated that the third index, J is not superfluous, although because of relationship (3) if two of U, V and J are known then the third can be simply calculated, so that J is superfluous in the same sense as the third index, i of the face index (hkil).

The derivation of Weber zone symbols can be described as follows*. We wish to define a zone axis, OP in terms of unit translations along each of the four crystallographic axes, to give a symbol of the form $\angle \bar{U}VJ\bar{W}$:

$$\text{viz: } OP = U \alpha_1 + V \alpha_2 + J \alpha_3 + W \alpha_4$$

When OP is defined in terms of only two of the three horizontal axes, giving a symbol $\angle \bar{u}v\bar{w}$, we obtain: $OP = u \alpha_1 + v \alpha_2 + w \alpha_4$

$$\text{But } \alpha_1 + \alpha_2 + \alpha_3 = 0 \\ \therefore \alpha_3 = -(\alpha_1 + \alpha_2)$$

* based upon Weber (1922), p.201.

So that $U\alpha_1 + V\alpha_2 - J(\alpha_1 + \alpha_2) + W\delta = u\alpha_1 + v\alpha_2 + w\delta$

rearranging this expression we obtain -

$$\alpha_1(U-J) + \alpha_2(V-J) + W\delta = u\alpha_1 + v\alpha_2 + w\delta$$

$$\therefore u = U-J$$

$$v = V-J$$

$$w = W$$

if we stipulate that $U + V + J = 0$

it follows that $J = -(U+V)$

$$\text{and} \quad \alpha_1(2U+V) + \alpha_2(2V+U) + W\delta = u\alpha_1 + v\alpha_2 + w\delta$$

$$\text{so that} \quad U = \frac{2u-v}{3} \quad (\equiv U = u - (u+v)/3)$$

$$V = \frac{2v-u}{3} \quad (\equiv V = v - (u+v)/3)$$

$$J = -\frac{u+v}{3}$$

$$W = w$$

Consequently when $u+v = 3n$ W will be equal to w but when $u+v \neq 3n$ then $W = 3w$, because of the need to maintain whole numbers in the zone symbol.

Weber showed that for a face $(hkil)$ lying in the zone $\angle \overline{UVJW}$ the assumption that $U+V+J = 0$ led to the useful relationship that -

$$hU + kV + iJ + lW = 0$$

thus justifying the original assumption.

Berman (1952), who examined material collected at Asbestos, Quebec, seems to have been the first to report an extensive investigation (including the application of x-ray diffraction techniques) into nemalite. The results of further x-ray and optical studies were published by Garrido (1936), by Tajder and Jong in 1938 (see Mineralog. Abstr. 7 360), by Fackler (1945) and by Eckhardt (1956), in the course of a study of "schweizerite".*

* The fibre photographs published by Eckhardt indicate that the material termed by him "schweizerite" exhibits the features here taken to be characteristic of Povlen-type chrysotile. Similarly labelled material, from the Oxford University Museum collection of minerals, was also found to exhibit these features; see chapter two.

TABLE 4.1

Symbols of some zone axes in the hexagonal system

<u>Direction</u>	<u>3-figure symbol</u>	<u>Weber 4-figure symbol</u>
a_1	$[100]$	$[2\bar{1}10]$
$\bar{a}_1$	$[\bar{1}00]$	$[\bar{2}110]$
a_2	$[010]$	$[\bar{1}2\bar{1}0]$
$\bar{a}_2$	$[0\bar{1}0]$	$[1\bar{2}10]$
a_3	$[\bar{1}10]$	$[\bar{1}\bar{1}20]$
$\bar{a}_3$	$[110]$	$[11\bar{2}0]$
ortho-hexagonal b-axes	($[210]$	$[10\bar{1}0]$
	($[120]$	$[01\bar{1}0]$
	($[\bar{1}10]$	$[\bar{1}100]$
	($[\bar{2}\bar{1}0]$	$[\bar{1}010]$
	($[\bar{1}\bar{2}0]$	$[0\bar{1}10]$
	($[1\bar{1}0]$	$[1\bar{1}00]$
	($[110]$	$[1100]$

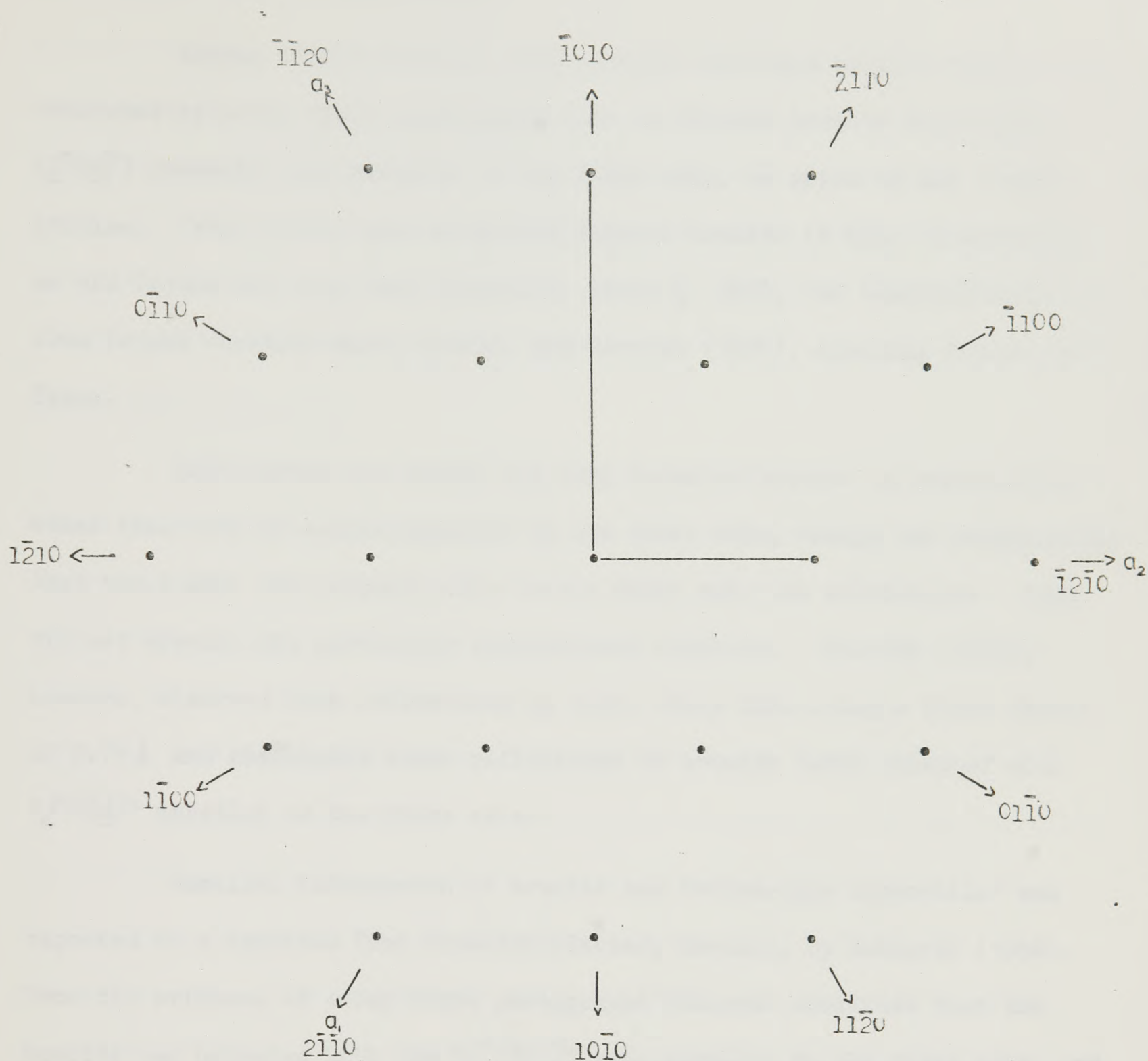


Figure 4.4. Zone symbols (Weber) for some zone axes in the hexagonal system.

More recently Liebling and Langer (1972) have reported the results of a combined x-ray and electron diffraction investigation of fibrous brucites associated with chrysotile, from Asbestos, Quebec. They also gave optical and chemical data in their paper.

Berman (1932) inferred from optical data (see section 4.2.3) and confirmed by x-ray fibre photographs that in fibrous brucite the a-axis ($\angle 100$) commonly lies parallel to the fibre axis, as noted in the present studies. West (1934) also mentioned fibrous brucite in this orientation, as did Tajder and Jong (see Mineralog. Abst. 7 360), who examined material from Lojane chromite mine, Serbia, and Garrido (1936), studying fibres from Texas.

Both Berman and Tajder and Jong detected brucite in orientations other than with an a-axis parallel to the fibre axis, though the relationship that the c-axis was perpendicular to the fibre axis was maintained. They did not specify the particular orientations observed. Garrido (1936), however, observed weak reflections on layer lines indicating a fibre repeat of $2.74 \text{ \AA}$ and attributed these reflections to brucite laths oriented with " $\angle 11\bar{2}0$ " parallel to the fibre axis.

Parallel intergrowth of brucite and Povlen-type chrysotile* was reported in a specimen from Findelen Glacier, Zermatt, by Eckhardt (1956). From the evidence of x-ray fibre photographs Eckhardt concluded that the brucite was oriented with the " $\angle 1\bar{1}0$ " axis parallel to the fibre axis, and hence parallel to the a-axis of chrysotile. He observed the identity period along the fibre axis to be $\sim 5.5 \text{ \AA}$, compared with $5.40 \text{ \AA}$, which he calculated for the " $\angle 1\bar{1}0$ " axis. Eckhardt was probably referring to the orthohexagonal b-axis $\angle 1\bar{1}00$ (equivalent to $\angle 1\bar{1}0$ in the three figure notation).

It is not altogether clear which axis was intended, by Garrido, but it is thought likely that he too was referring to a fibre axis lying parallel to an orthohexagonal b-axis, along which the repeat distance is $a\sqrt{3}$ ($\approx 5.4 \text{ \AA}$).

* See footnote to page 125.

Garrido's reference to material oriented with an axis $"/\bar{1}1\bar{2}0/$ " parallel to the fibre axis and giving an axial repeat of $\sim 2.7\text{\AA}$ must be in error. Such a symbol, which must presumably be interpreted as a Weber four-figure symbol, refers to the negative direction of the a_3 crystallographic axis (see Table 4.1). The repeat along such an axis would clearly be $\sim 3.1\text{\AA}$. Similarly his reference to a zone axis $"/\bar{1}0\bar{1}0/$ " as giving an identity period of $3.15\text{\AA}$ is also in error since this refers as a four figure basis to an ortho-hexagonal b-axis which would give an axial repeat of $\sim 5.4\text{\AA}$. It may simply be that Garrido's zone axis symbols for the two orientations have been transposed in error.

4.2.3 Optical Features

In a polarising microscope the disaggregated fibres of nemalite appear to be lath-like (Berman, 1932) and this is confirmed by observation in the electron microscope. The laths exhibit parallel extinction and are length fast. Since brucite is uniaxial positive the fibre axis cannot be parallel to the c-axis (equivalent to the χ refractive index), which led Berman to assume the optic orientation illustrated in figure 4.3a.

The birefringence, δ of the fibres is generally too low (relative to δ observed on tabular crystals of brucite), which contributes to the difficulties of recognition of fibrous brucite in thin sections of serpentinites. This feature was noted by Berman and investigated further by Donnay (1944). Berman measured the refractive indices of laths in the X direction (figure 4.3) obtaining a value of 1.585, considerably in excess of the usual value of w in brucite (e.g. 1.566 is quoted by Donnay). This high value was attributed by Berman to the high degree of iron substitution. Liebling and Langer (1932) obtained a mean value for w of 1.576, on laths selected for their near isotropic character, they too attributed the high value to substitution by iron (and manganese) for magnesium in the structure.

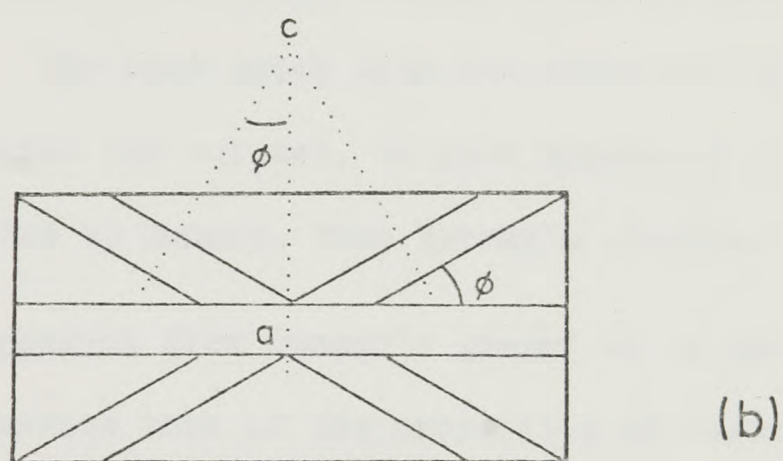
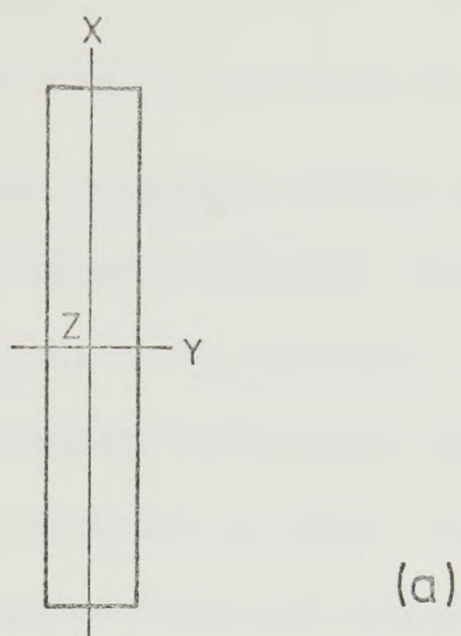


Figure 4.5. (a). Optical orientation of brucite laths.

(b). Idealised cross-section through brucite fibres
to show the relation of individual crystals.

(After Berman 1932, figures 4 and 5).

Donnay (1944), however, examined material similar to that studied by Berman and expressed doubt as to whether the effect of iron substitution could be wholly responsible for the high w value. This view was supported by his calculation of a value of 1.570 for the w index of brucite, with the composition implied by the chemical analysis given by Berman (section 4.2.1).

From x-ray powder photographs Donnay demonstrated the presence of magnetite (as well as very minor periclase), which he considered was suggested also by observations in the electron microscope, though not apparent optically. Weissenberg photographs showed the fibres to possess rotational symmetry. On the basis of these observations Donnay thought that an individual fibre of nemalite (observed optically) could be "considered as a uniaxial entity with its optic axis in the direction of elongation" (p.11). He was then able to apply the formulae of "form birefringence" (in particular "rod birefringence"). These permit the calculation of w and ϵ in a uniaxial substance containing varying proportions of "interstitial material" (in this case magnetite). The best match with the observed refractive indices was for $\sim 1.5\%$ magnetite (by volume), in good agreement with the proportion of magnetite calculated by Donnay, from Berman's chemical analysis.

It is apparent from Donnay's graphs of w and ϵ vs. volume percentage of magnetite that if the proportion of magnetite exceeds a value of $\sim 3.1\%$ then ϵ becomes greater than w and the fibres would be expected to be length slow. No such fibres were observed by Donnay, nor do there seem to be any reported instances of length slow brucite fibres. Their recognition during routine examination of serpentinites is, however, unlikely since chrysotile is length slow, so that because of the frequent lack of any obvious optical distinction between brucite and chrysotile, any length slow fibres would generally be termed chrysotile.

Another commonly observed optical anomaly of fibrous brucite is apparent on examination of the interference figures from apparently single laths (Berman, 1932). The figure is biaxial positive with widely ranging

values of 2V. Berman measured a 2V of 70° , Tajder and Jong (1938) reported values of $54-59^\circ$, while Fackler (1945) reported values ranging from $30-70^\circ$, most commonly about 35° . Liebling and Langer (1972) obtained diffuse biaxial figures but did not determine 2V. On the basis of Donnay's interpretation of the optical character of nemalite fibres we would expect a uniaxial flash figure, rather than a centred biaxial figure. His explanation cannot then, be altogether correct.

4.2.4 Interpretation

In seeking an explanation for the fibrous habit of brucite, Berman noted the structural similarity between the brucite and chrysotile structures in their respective a-axis directions (see figure 4.6). He suggested that the similarity might be "sufficiently close for the brucite to replace the chrysotile most readily along that direction" (p.515).

Berman noted that Poitevin and Graham (1918) had advanced a similar interpretation of fibrous brucite associated with asbestos from the Thetford area, Quebec.

From figure 4.6 it is apparent that a better structural match would be achieved between the hydroxyl sheets of brucite and chrysotile, if one or other phase were to be rotated through ninety degrees. Clino- and ortho-chrysotile are inherently curved about the a-axis so that this axis is of necessity, parallel to the fibre axis. In this case then, the brucite must take on a 'new orientation' to bring an ortho-hexagonal b-axis parallel to the fibre axis. The several reported occurrences of brucite in this orientation can presumably be attributed to attempts to achieve this better match with the chrysotile structure.

The observation of intergrowths of brucite (a-axis parallel to the fibre axis) and para-chrysotile during the present studies provides evidence of an alternative mechanism by which the best match of the hydroxyl sheets of

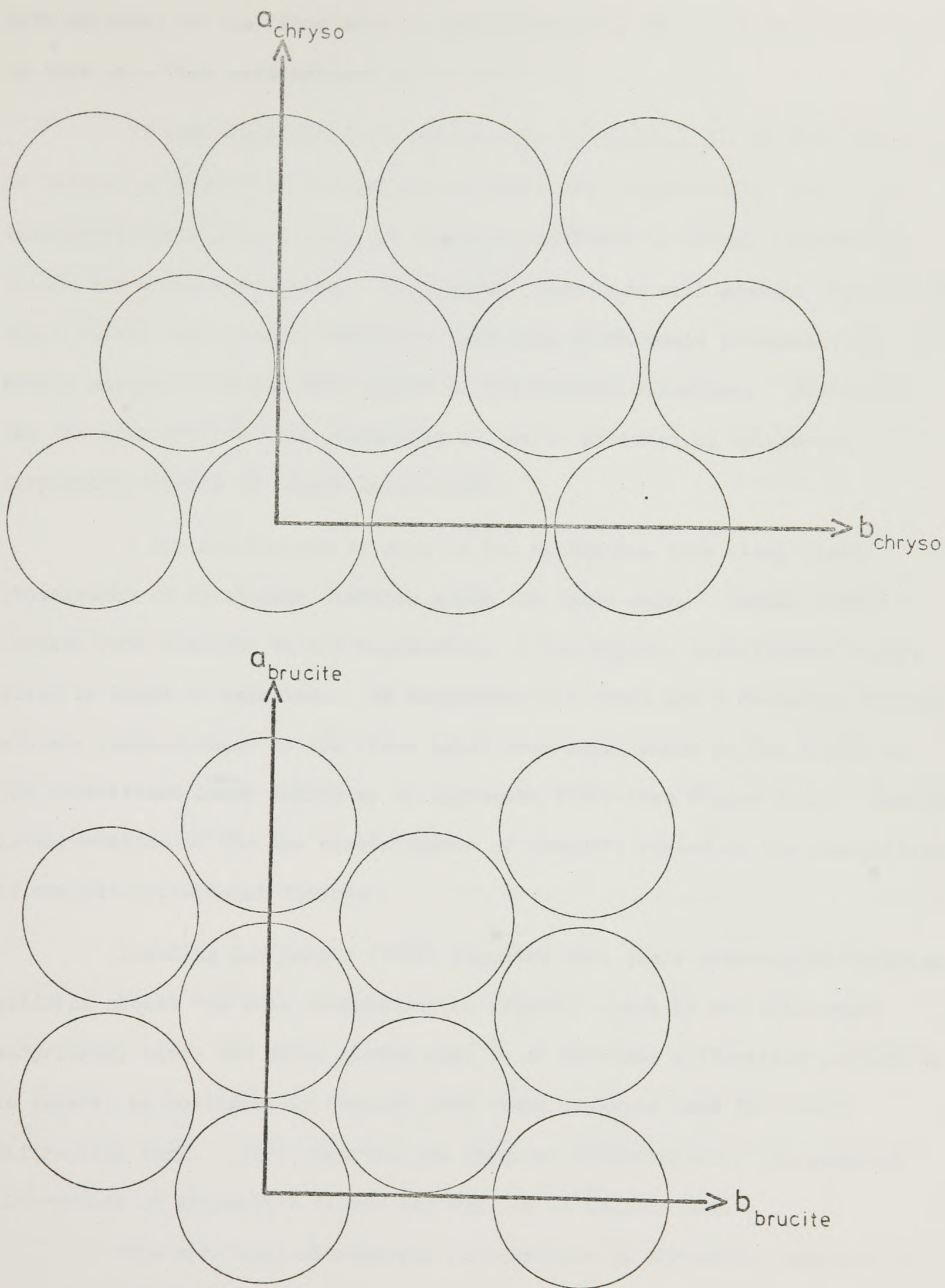


Figure 4.6. Diagrams to illustrate the relationship between basal hydroxyls in brucite and chrysotile. See text for discussion.

brucite and chrysotile may be achieved. Since the b-axis of chrysotile lies parallel to the fibre axis in para-chrysotile the requirement for brucite to take on a "new orientation" is obviated*.

If para-chrysotile and Povlen-type chrysotile are in fact polygonal in nature, as suggested in chapters two and three respectively, then their intergrowth with brucite will be favoured, relative to normal cylindrical clino- and ortho-chrysotile. A polygonal structure will present essentially flat, rather than curved, sheets of hydroxyls which would presumably be more easily matched with the flat layers of the brucite structure. Similarly, the fit with brucite will presumably be better achieved by cylindrical chrysotile fibrils of larger outer radii.

A further feature of note is the indication from x-ray fibre photographs of rotational disorder about the fibre axis. Berman (1932) invoked such disorder in his explanation of the biaxial interference figure given by laths of nemalite. He suggested that there was a deviation (within a plane perpendicular to the fibre axis) from parallelism of the c-axes of the constituent laths making up an aggregate fibre (see figure 4.5). Donnay's interpretation of the low birefringence of nemalite rested on the recognition of complete rotational disorder.

Liebling and Langer (1972) reported that their electron diffraction patterns showed "no such disorientation effect", which is not altogether surprising, since the units giving rise to an electron diffraction pattern will in general be considerably smaller than those crystals used for x-ray diffraction work. They reported the frequent observation of the parallel intergrowth of chrysotile fibres and went on to suggest that -

"The sub-light microscopic intergrowths of chrysotile parallel to the lath fibre axis can account for the observed disorder in the relatively large laths which, although they appear to be single crystals, are in truth aggregates of crystals". (p.862).

* As a possible converse of this it may be that the development of the para-chrysotile variety is encouraged by intergrowth of chrysotile with brucite laths. This might account for the unusual abundance of para-chrysotile in specimen AG 67.761 (see chapter three section 3.3.3)

Liebling and Langer do not discuss this model in any great detail and its physical nature is not altogether clear. In the light of some further comments in their paper, it is thought that they intended to imply that included chrysotile fibrils prevent the parallelism of successive brucite laths. Liebling and Langer do not themselves seem to be altogether satisfied by this model for they offer an alternative explanation (which they consider at this stage to be less reasonable, and for which there seems to be no evidence) for the optical and diffraction phenomena observed -

"Brucite's changed morphology may reflect a more fundamental structural modification. . . . the biaxial figure may reflect the existence of a lower symmetry structural polymorph of brucite". (pp. 862-863).

In view of the rotational symmetry (about the fibre axis) of all chrysotile fibrils it is not surprising that the brucite reflections on x-ray fibre photographs (of brucite/chrysotile intergrowths) show evidence of rotational disorder. Rather, it would perhaps be expected that the electron diffraction patterns would show on occasion, some similar evidence of partial disorder (but see above).

The interpretation of brucite/chrysotile intergrowths here favoured is in terms of a model similar to that initially put forward by Berman and modified by Liebling and Langer, it is illustrated in figure 4.7. This model will account for the lath-like morphology of aggregate fibres when observed optically, and for the partial (or complete) rotational disorder about the fibre axis, apparent in x-ray photographs. In the electron microscope the disaggregated constituents of the brucite/chrysotile intergrowths will generally be observed (i.e. isolated brucite laths and chrysotile fibrils), with occasional aggregate laths.

The model proposed also provides a qualitative explanation for the variable biaxiality of the aggregate laths, much as in Berman's (1932) interpretation. The constituent brucite units are in parallel orientation

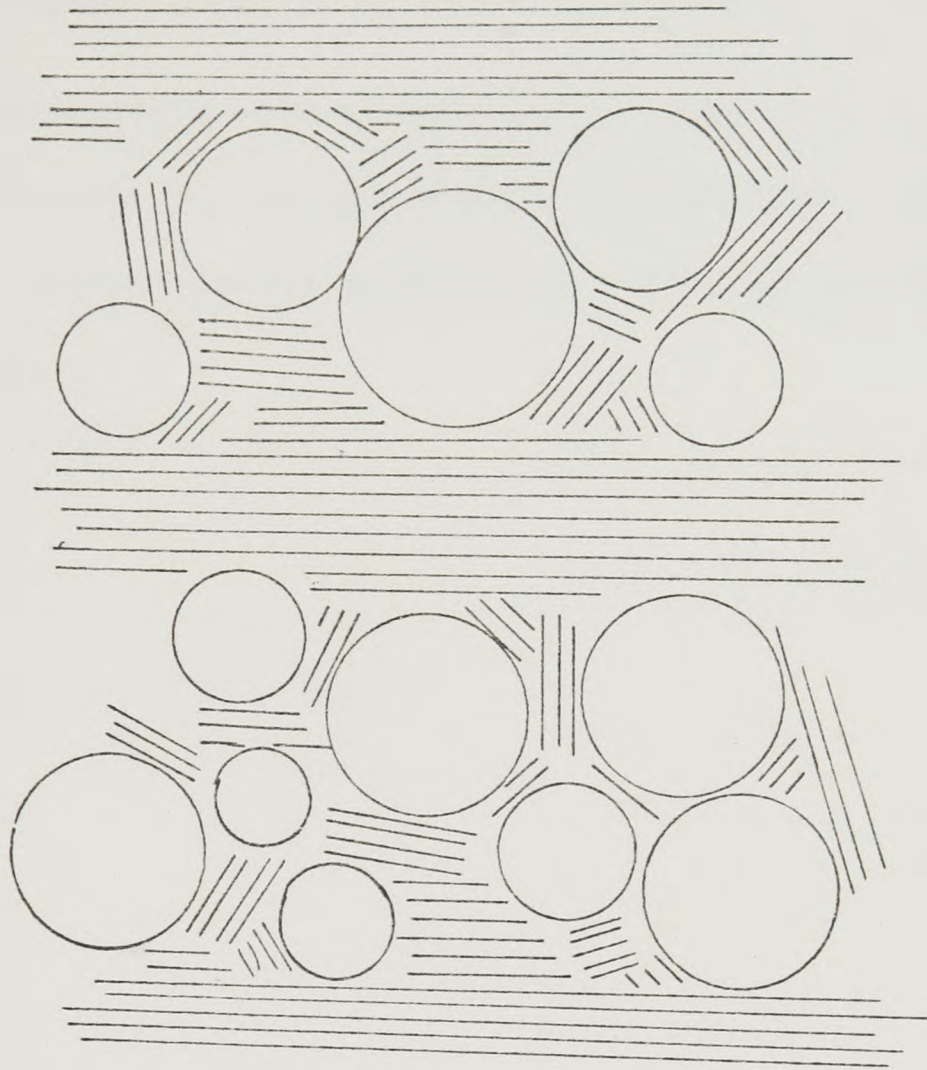


Figure 4.7. Schematic representation of the proposed model for brucite-chrysotile intergrowths.

with respect to their a-axes so that the refractive index in the lath axis direction will be w (see figure 4.5). The refractive indices in the Z and Y directions will, however, take on values intermediate between w and ϵ (Z somewhat less than ϵ , Y somewhat greater than w), dependent upon the make-up of the particular lath. Thus, the value of $2V$ will be variable between different laths, according to the resultant values of β and γ

Intergrowth with chrysotile is probably an important, if not essential feature, in the development of nemalite. Para-chrysotile and Povlen-type chrysotile are probably of particular importance in these intergrowths.

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CHAPTER FIVE

The hydroxycarbonates and related minerals

Several minerals, all of which have apparently been produced during the secondary alteration of serpentinites and which are closely related to brucite, have been reported. Because of common features in their modes of occurrence, chemistry and crystal structures, discussion of these minerals is here brought together under the rather indefinite heading of "hydroxycarbonates and related minerals".

After some discussion of the chemical and structural features exhibited by these minerals, the stability of brucite in the weathering environment and the occurrence of the hydroxycarbonates and related minerals is reviewed. Finally, some observations made during the present studies will be reported.

5.1 Chemical and structural features

Pyroaurite gives its name to a group of three minerals established by Frondel (1941). The members of this group have three-layer, rhombohedral (3R) structures and are poly typic with a group of three hexagonal minerals with two-layer (2H) structures, termed by Frondel the sjogrenite group. A general formula, applicable to both of these groups of minerals was given by Frondel as $Mg_6 R_2(OH)_{16} CO_3 \cdot 4H_2O$, where R can be Fe^{III} , Al^{III} or Cr^{III} , as indicated in Table 5.1.

In a recent review of the crystal structures of 'double hydroxide' minerals Taylor (1973) included two additional minerals, reevesite and eardleyite, in the pyroaurite group. In these two minerals the divalent cation is Ni^{II} , in place of Mg^{II} and R is Fe^{III} and Al^{III} in reevesite and eardleyite respectively. Their inclusion in the pyroaurite group necessitates a more general formula: $M_6^{II} M_2^{III} (OH)_{16} CO_3 \cdot 4H_2O$.

Brown and Gastuche (1967) put forward a possible structural interpretation of the hydroxycarbonates. They suggested that all the cations are situated in brucite-type layers, giving rise to an overall positive charge, which is balanced by negatively charged interlayers, consisting of CO_3^{--} and H_2O . Their ideas were confirmed by several x-ray investigations, particularly of pyroaurite, reported by Allmann and Lohse (1966), Ingram and Taylor (1967) and by Allmann (1968, 1969).

The cations occur in octahedral sites in the brucite-type layers, $\left[(\text{Mg}, \text{Fe}^{III}) (\text{OH})_2 \right]^{.25+}$, which form the backbone of the structure. These layers are approximately 4.9 Å thick in the c-axis direction, whereas the distance between two adjacent layers was found by Allmann (1968) to be $c/3 = 7.8 \text{ Å}$. The 2.9 Å "spaces" are occupied by disordered "liquid-like" interlayers, $\left[\frac{1}{6} \text{CO}_3^{--} + \frac{1}{2} \text{H}_2\text{O} \right]^{.25-}$.

Taylor (1969) demonstrated that there is some degree of ordering of magnesium and iron in the octahedral layer, to the extent that in some crystals, regions which are almost iron-free seem to occur. In order to represent this ordering Taylor (1973) wrote the structural formula for the pyroaurite-sjogrenite minerals as $\left[\bar{\text{M}}_{1-X}^{II} \text{M}_X^{III} (\text{OH})_2 \right] (\text{CO}_3)_{X/2} (\text{H}_2\text{O})_{1-\frac{3X}{2}} - \Delta$ "Where Δ is below about .125 and X probably has a maximum value of .53", and a minimum of zero. Naturally occurring minerals of the pyroaurite-sjogrenite groups commonly have at any rate an average value of $X = 0.25$; the reason for this is not known.

A recently recognised mineral, named coalingite from the type locality Coalinga, California, was described by Mumpton, Jaffe and Thompson (1965) from the New Idria serpentinite. They gave its composition as $\text{Mg}_{10} \text{Fe}_2^{III} (\text{CO}_3) (\text{OH})_{24} 2\text{H}_2\text{O}$. A second occurrence of coalingite was reported by Jambor (1969a) who gave a chemical analysis, which he interpreted in terms of a formula, slightly different to that of Mumpton et al (1965): $\text{Mg}_{8.31} \text{Fe}_2^{III} (\text{CO}_3)_{.58} (\text{OH})_{22.06} \text{H}_{1.35} \text{O}_{1.51}$. Jambor's

TABLE 5.1

Some hydroxycarbonate and related minerals
(modified from Taylor (1973), p. 378)

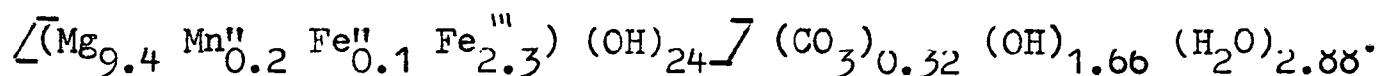
<u>Idealised formula</u>	<u>Name</u>	
	<u>3R polytype</u>	<u>2H polytype</u>
$\text{Mg}_6\text{Fe}^{\text{III}}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$	Pyroaurite*	Sjogrenite*
$\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$	Hydrotalcite*	Manasseite*
$\text{Mg}_6\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$	Stichtite*	Barbertonite*
$\text{Ni}_6\text{Fe}^{\text{III}}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$	Reevesite	-
$\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$	Eardleyite	-
$(\text{Ni},\text{Co},\text{Fe})_8(\text{OH})_{16}(\text{OH},\text{S},\text{H}_2\text{O})_8$	Jamborite	-
$\text{Mg}_{6.2}\text{Fe}^{\text{III}}_{1.8}(\text{OH})_{16}\text{Cl}_{1.624}(\text{H}_2\text{O})_{4.8}$	Iowaite	-
$\text{Mg}_{10}\text{Fe}^{\text{III}}_2(\text{OH})_{24}(\text{CO}_3)_2\text{H}_2\text{O}$	Coalingite	-
$\text{Mg}_{16}\text{Fe}^{\text{III}}_2(\text{OH})_{36}(\text{CO}_3)_2\text{H}_2\text{O}$	Coalingite-K	
$\text{Mg}_{6.8}\text{Fe}^{\text{III}}_4(\text{O}_{3.8}(\text{OH})_{18})(\text{H}_2\text{O})_{1.3}$	Muskoxite	

Hexagonal cell parameters -

$a_{\text{H}} \approx 3.1 \text{ \AA}$ for all minerals
 $c_{\text{H}} \approx 23.4 \text{ \AA}$ for 3R polytypes, except
coalingite and iowaite
 $\approx 15.6 \text{ \AA}$ for 2H polytypes
 $\approx 37.4 \text{ \AA}$ for coalingite
 $\approx 24.25 \text{ \AA}$ for iowaite
unknown for coalingite-K and
muskoxite

* minerals included by Frondel (1941) in the pyroaurite and sjogrenite groups.

interpretation of his chemical data can, however, be criticised on several counts. Pastor-Rodriguez and Taylor (1971) noted the fundamental point that the formula given by Jambor does not balance; it has an overall negative charge of 1.87. The inclusion of non-stoichiometric water of crystallisation in the formula and Jambor's contention that a part of the weight loss on ignition, should be attributed not to H₂O and CO₂, but to adsorbed heavy liquids used in the separation procedure are also of doubtful validity. Pastor-Rodriguez and Taylor re-interpreted Jambor's chemical analysis in terms of the formula:



The structure of coalingite was determined using single crystal x-ray methods by Pastor-Rodriguez and Taylor. They found that it is trigonal, with $a_H = 3.12 \text{ \AA}$ and $c_H = 57.4 \text{ \AA}$. Coalingite exhibits a good cleavage parallel to (0001). The structure is of a layer type similar to that of pyroaurite. The idealised sequence of layers is illustrated in figure 5.1, where it is compared with the sequences in several related minerals. The magnesium and iron cations (and presumably the manganese cations also) are in octahedrally co-ordinated sites in a brucite-type layer. Two such layers are present in each 'elementary unit' and associated with these is a disordered layer, which contains the CO₃²⁻ anions and water molecules (together with some OH groups in the material described by Jambor).

Pastor-Rodriguez and Taylor also investigated the structure of coalingite-K, which was described by Mumpton et al (1965) as a variant of normal coalingite, on the basis of its x-ray powder pattern. They concluded that this variety possesses a structure similar to that of normal coalingite, but with three brucite-type layers instead of two in the elementary unit. This gives rise to an increased c parameter of 17.2 Å (cf 12.5 Å for coalingite), so that the prominent spacings at 5.72 Å and 4.38 Å observed by Mumpton et al might be explained as third and fourth order basal reflections,

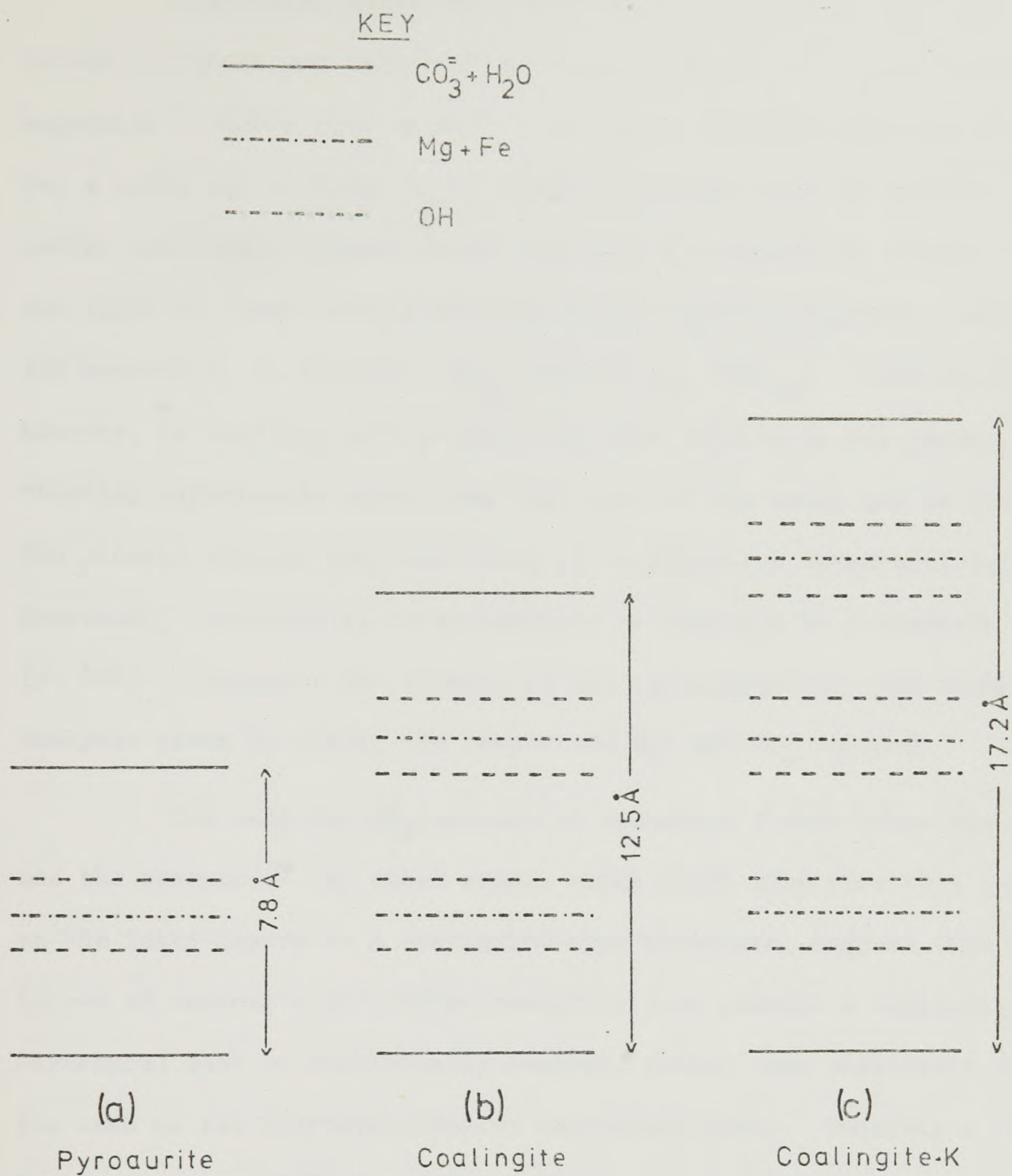


Figure 5.1. Sequences of layers in some hydroxycarbonate minerals,
(after Pastor-Rodriguez and Taylor 1971, figure 1).

respectively. On the basis of this model the ideal formula for coalingite-K is $\text{Mg}_{16} \text{Fe}_2^{\text{III}} (\text{OH})_{36} (\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (Pastor-rodriguez and Taylor, 1971).

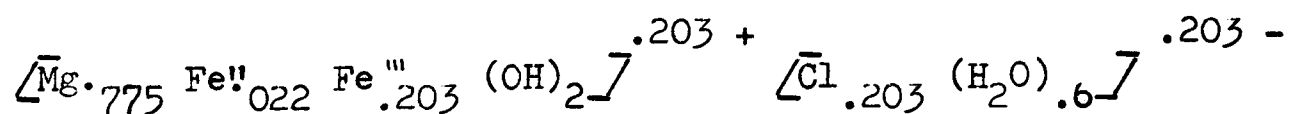
Muskoxite, named for its occurrence in serpentinites of the Muskox intrusion was described by Jambor (1969b) as "a new hydrous magnesium - ferric iron oxide". He gave a chemical analysis ($\text{Fe}_2\text{O}_3 = 41.1\%$, $\text{Feo} = 0.0\%$, $\text{MgO} = 35.4\%$, $\text{H}_2\text{O} = 23.8\%$), together with an infrared spectrum, powder and single crystal x-ray data and the results of thermal studies. In the light of these various investigations Jambor presented a tentative formula for muskoxite, as follows - $\text{Mg}_{3.4} \text{Fe}_2^{\text{III}} (\text{CO}_3)_{<1} (\text{OH})_{12}$. This formula is, however, in conflict with a statement made earlier in his paper, that "heating experiments have shown that part of the water can be driven out of the mineral without any indication of an attendant structural collapse. Presumably therefore it is appropriate to show H_2O as a discrete entity" (p. 686). Moreover the formula is not consistent with the chemical analysis given by Jambor (in respect of H_2O and CO_2 values).

The very low CO_2 content of muskoxite ("much below one percent") and the absence of any other anion, which might give rise to a negative charge on the inter-layers of a coalingite-type structure, suggest that the brucite-type layers of muskoxite (if indeed muskoxite does possess a coalingite-type layer structure) must be electrically neutral, rather than positively charged, as is the case in the hydroxycarbonates described above. Possibly a formula of the type: $\text{Mg}_{6.8} \text{Fe}_4^{\text{III}} (\text{O}_{3.8} (\text{OH})_{18}) (\text{H}_2\text{O})_{1.3}^*$ is more appropriate. Further investigation of muskoxite is required before its nature can be fully appreciated.

The mineral iowaite is closely related structurally to pyroaurite. It was described by Kohls and Rodda (1967) as an oxychloride, with a formula $4\text{Mg}(\text{OH})_2 \text{FeOCl} \cdot x\text{H}_2\text{O}$, where $x \leq 4$ but this interpretation was disputed by

* This formula was derived by recalculation of Jambor's chemical analysis, assuming that water expelled below 200°C in the heating experiments (2.45%) represented discrete water molecules, leaving 21.35% structural H_2O .

Allmann and Donnay (1969). They considered that iowaite is probably isostructural with pyroaurite and gave the structural formula as -



Kohls and Rodda determined the hexagonal unit cell parameters of iowaite as $a_H = 3.119\text{\AA}$ and $c_H = 24.25\text{\AA}$ which led Allmann and Donnay to suggest that the unit of structure consists of three brucite-type layers associated with three interlayers, containing the chlorine anions and water. Kohls and Rodda demonstrated that the water could be removed by heating to 280°C , without destroying the layer structure. Allmann and Donnay inferred from this that the interlayers are 'liquid-like', as in pyroaurite; they suggested that collapse of the layer structure on heating was prevented by the chlorine anions, remaining after removal of the water.

In 1964 Jambor and Boyle reported an un-named nickel hydroxide mineral, from serpentinites in British Columbia. Apparently similar material was described in greater detail by Lapham (1965). The material which he studied was rhombohedral with $a_H = 3.12\text{\AA}$ and $c_H = 23.19\text{\AA}$ (more rarely $c_H = 23.79\text{\AA}$). Lapham considered that its structure was closely related to that of brucite, and suggested that it might in fact be a nickeliferous poly type of brucite. However, his suggestion that the mineral might consist of units of $\frac{1}{4}(\text{Ni},\text{Fe})\text{O},\text{OH}$ embedded within the lamellae of a $\text{Mg}(\text{OH})_2$ brucite-type rhombohedral structure, conflicts with this view. Furthermore, Lapham thought it possible that CO_3^{--} and water of crystallisation played essential roles in the structure, which would also invalidate any poly typic relationship with brucite.

It seems more likely that this mineral is related structurally to the 3R hydroxycarbonates described above (on the basis of its c unit cell parameter); in particular it may be related to reevesite. This view is supported by a recent paper describing a new mineral, jamborite (named for Jambor), which is essentially a nickel hydroxysulphide (Morandi and Dalrio, 1973).

In this paper it is suggested that the structure of jamborite can be interpreted in terms of the same scheme as that adopted for the hydroxycarbonates, described above. The elementary unit is 7.8Å thick and consists of positively charged, octahedral, brucite-type layer containing Ni, Co and Fe cations and a negatively charged sheet containing OH and S anions. Morandi and Dalrio gave an idealised formula for jamborite: $(\text{Ni, Co, Fe})_{1-X}^{II} (\text{Ni, Fe})_X^{III} (\text{OH})_2 \left[\bar{2}(\text{OH}), \bar{S} \right]_{.5X} (1-.5X)\text{H}_2\text{O}$. This is very similar to the general formula given by Taylor (1973) for the pyroaurite-sjogrenite group minerals (see above). On this basis jamborite possesses a 5R type structure ($c_H = 23.3\text{\AA}$).

Morandi and Dalrio noted that the x-ray powder pattern of jamborite was similar to those of the specimens described by Jambor and Boyle (1964) and Lapham (1965) and to the pattern of reevesite. "The name 'jamborite' is intended to include the minerals both from Italy (Morandi and Dalrio) and from British Columbia (Jambor and Boyle)" (Morandi and Dalrio, 1973; p. 837). Differences (between jamborite and other material) in respect of the relative intensities of x-ray reflections were attributed by Morandi and Dalrio either to compositional differences or to stacking variations.

5.2 The stability of brucite in the weathering environment and the occurrence of the hydroxycarbonates and related minerals

The apparent susceptibility of brucite to alteration in the near surface environment, where carbon dioxide-bearing waters are circulating was commented on by Hostetler et al (1966). They stated that Hostetler (1960) had found that the conversion of brucite to hydromagnesite requires a partial pressure of CO_2 (PCO_2) of only 10^{-6} atmospheres. Hostetler et al considered that even lower values of PCO_2 are probably sufficient to bring about the conversion of brucite to pyroaurite or coalingite.

The stabilities of serpentine and brucite in low temperature weathering environments were investigated by Wildman, Whittig and Jackson (1971), as an indirect approach to the estimation of the relative stabilities of montmorillonite and saponite, in high magnesium soils derived from serpentinites. They calculated the apparent standard free energy of formation, ΔG_f° of serpentine* from solubility data for several Californian serpentinites and were then able to plot stability diagrams. These diagrams were similar to those used previously by Garrels and Christ (1965), and were based upon calculations using the value of -962.9 kcal./mole for ΔG_f° of serpentine and published free energy data for other phases.

One of the diagrams produced by Wildman et al is reproduced as figure 5.2. This diagram demonstrates the severely limited field of stability of brucite in a weathering type of environment.

At present free energy data are not available for most of the minerals described in the previous section, which precludes the calculation of the stability relationships between the various phases.

Pyroaurite is of fairly widespread occurrence in serpentinites - see for instance Meixner (1937). More recently Mumpton and Thompson (1966) reported pyroaurite and coalingite as products of the in situ weathering of Fe-brucite in the New Idria serpentinite. They gave a possible scheme by which these minerals might be produced -

* The average value of a ΔG_f° which Wildman et al obtained (-962.9 kcal./mole) agrees with that of Bricker, Nesbitt and Gunter (1973 who reported a value of -962 kcal./mole for the standard free energy of formation of chrysotile. These values are a few kilocalories less negative (implying a lower stability) than the value of ΔG_f° for chrysotile determined from dissolution experiments by Hostetler and Christ (1968). Bricker et al, however, criticised the interpretation of Hostetler and Christ, on the grounds that their assumption of congruent solution of chrysotile was probably erroneous. They based their criticism upon considerations of the variations in the Mg/Si ratio throughout the dissolution.

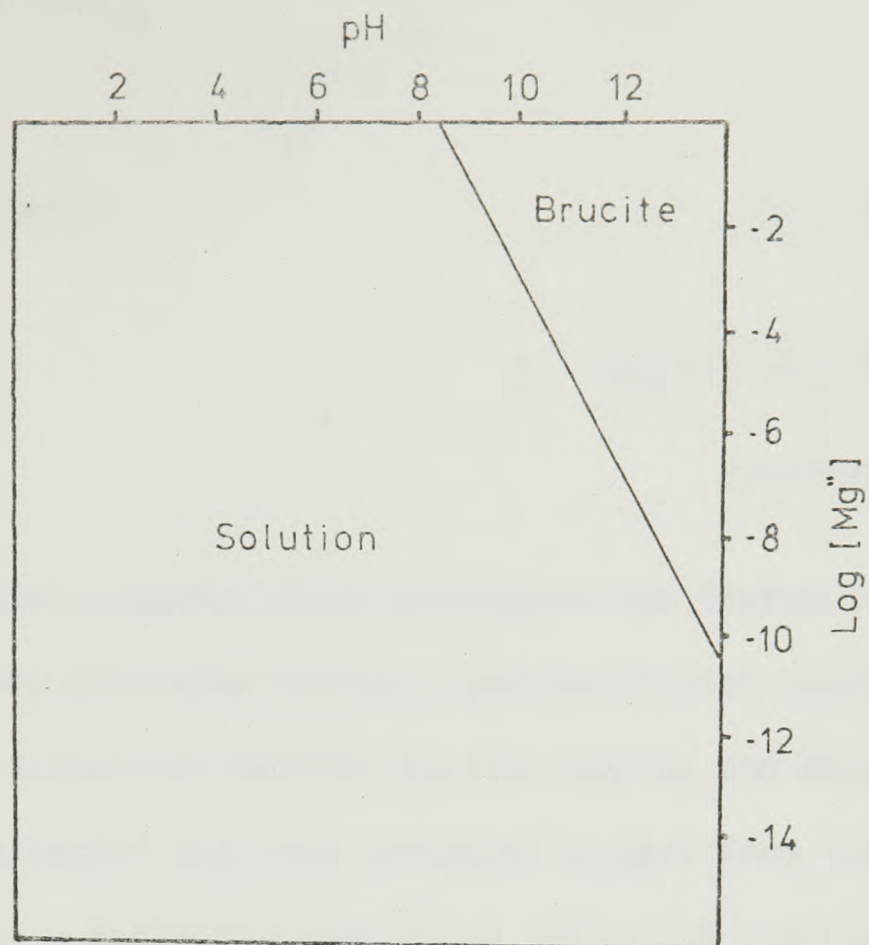
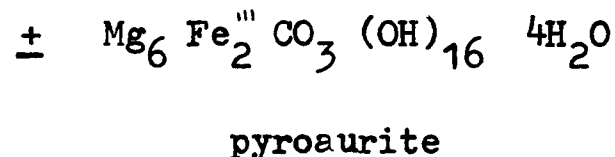
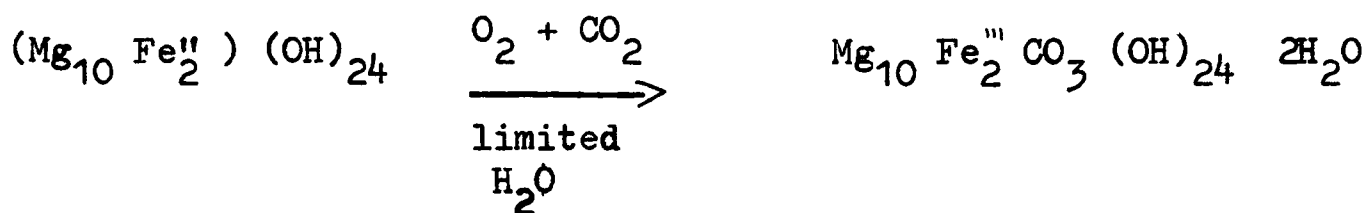


Figure 5.2. Stability of brucite expressed in terms of pH and activity of Mg²⁺ at 25°C and 1 atmosphere, (after Wildman et al 1971, figure 4).



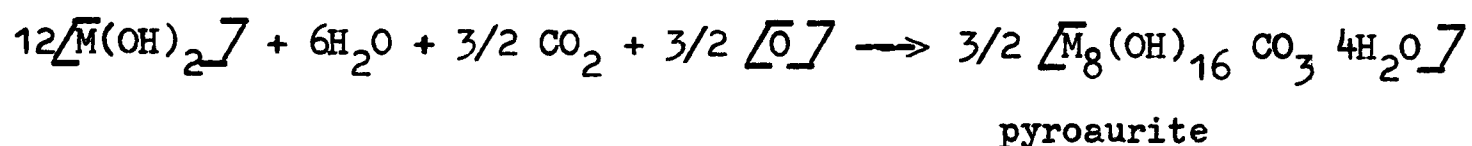
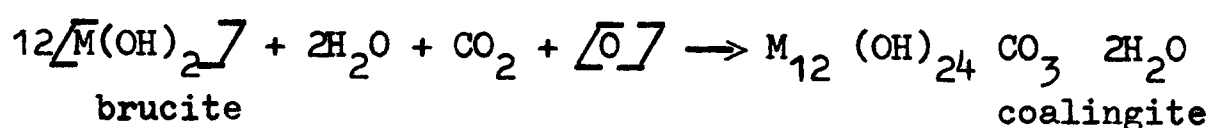
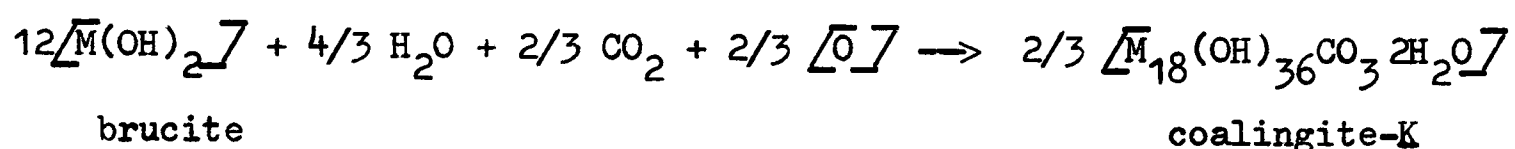
Jambor (1969a) reported that coalingite had formed in drill core samples from the Muskox intrusion during a period of five years' storage. He did not, however, detect any brucite in his samples and suggested that in this instance, coalingite had been produced in part from the alteration of pre-existing oxides - including muskoxite, which had been noted in the core material during logging (Jambor, 1969b) but mainly from the alteration of fibrous sulphides.

Jambor (1969a) considered that some of the fibres of coalingite which he observed, were in fact pseudomorphs after the fibrous iron sulphide mineral. The production of coalingite from this sulphide material is somewhat surprising, and must involve the introduction of magnesium from the alteration of some other phase (presumably a serpentine mineral, in the absence of brucite). Some light on the transformation of the sulphide phase to a hydroxycarbonate may be provided by observations on the formation of jamborite, which appears to involve a replacement of S^{2-} by OH^- (Morandi and Dalrio, 1973).

Jamborite is essentially a nickel hydroxysulphide and was observed by Morandi and Dalrio as pseudomorphs after millerite. Several stages in the transformation process from the sulphide to the hydroxysulphide were apparent and Morandi and Dalrio suggested that a gradual replacement of the sulphur in millerite might have occurred in response to more oxidising, hydrothermal conditions.

Pastor-Rodriguez and Taylor (1971) observed that coalingite has a lower Fe/Mg ratio than typical specimens of pyroaurite, and suggested that the latter might therefore be produced by the alteration of more iron-rich brucite, while coalingite would be produced from the iron-poor varieties.

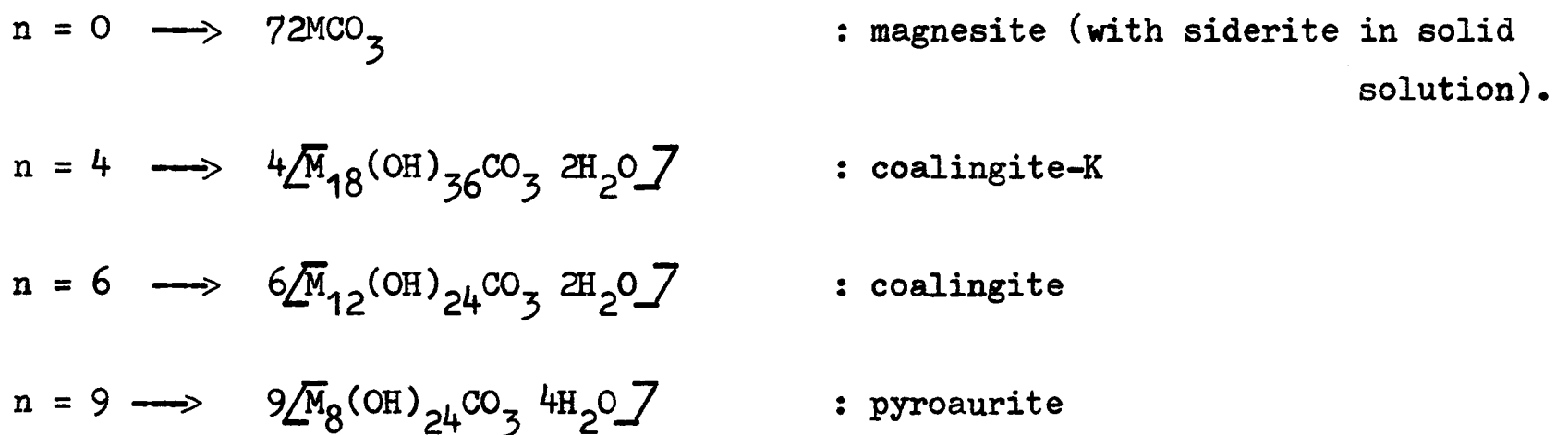
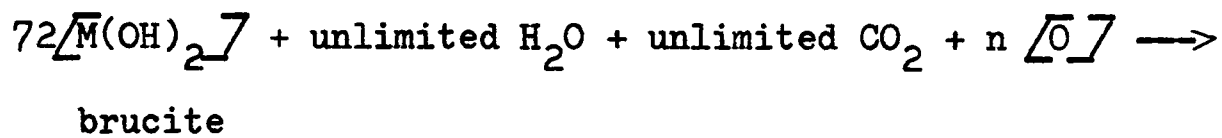
Taylor (1973) noted that in schemes of reaction such as those given below less water is required to form coalingite, relative to pyroaurite; it is also apparent that even less water is required to form coalingite-K. Taylor went on to suggest that coalingite might therefore form more readily than pyroaurite under conditions of limited water supply.



where M = Fe^{II} and Mg^{II} and Fe^{III}

From these equations it can be seen, however, that P O₂ and the availability of CO₂ will also influence which hydroxycarbonate is produced. It is likely that in veins and fissures (where the hydroxycarbonate minerals commonly occur) water and CO₂ will normally be present in excess of the amounts required to effect the "complete" alteration of Fe-brucite to pyroaurite, and that the eventual product will in fact depend mainly upon PO₂ and on the original composition of the brucite.

The relationships between the original brucite composition, degree of oxidation and the hydroxycarbonate produced are illustrated diagrammatically in figure 5.3. The sequence of minerals produced in response to increasing oxidation is shown below -



Where M = Fe^{II} and Mg^{II} and Fe^{III}

It may be that muskoxite is produced from Fe-brucite in response to conditions of very low PCO₂. In this context it is perhaps significant that Jambor (1969b) considered that muskoxite was a primary phase, occurring in freshly drilled serpentinite core material and that on exposure to the atmosphere it altered to coalingite.

Temperature can be a further factor which will influence the alteration of Fe-brucite. Allmann (1968) reported intergrowths of pyroaurite and sjogrenite, in which sjogrenite formed the cores of crystals. On the strength of this observation and other, experimental evidence he suggested that pyroaurite and the 3R polytypes in general are the low temperature polytypes in the pyroaurite-sjogrenite groups.

Iowaite was originally described from material occurring in veinlets cutting a Pre-Cambrian serpentinite (Kohls and Rodda, 1967). This mineral may be an important repository for chlorine in serpentinites.

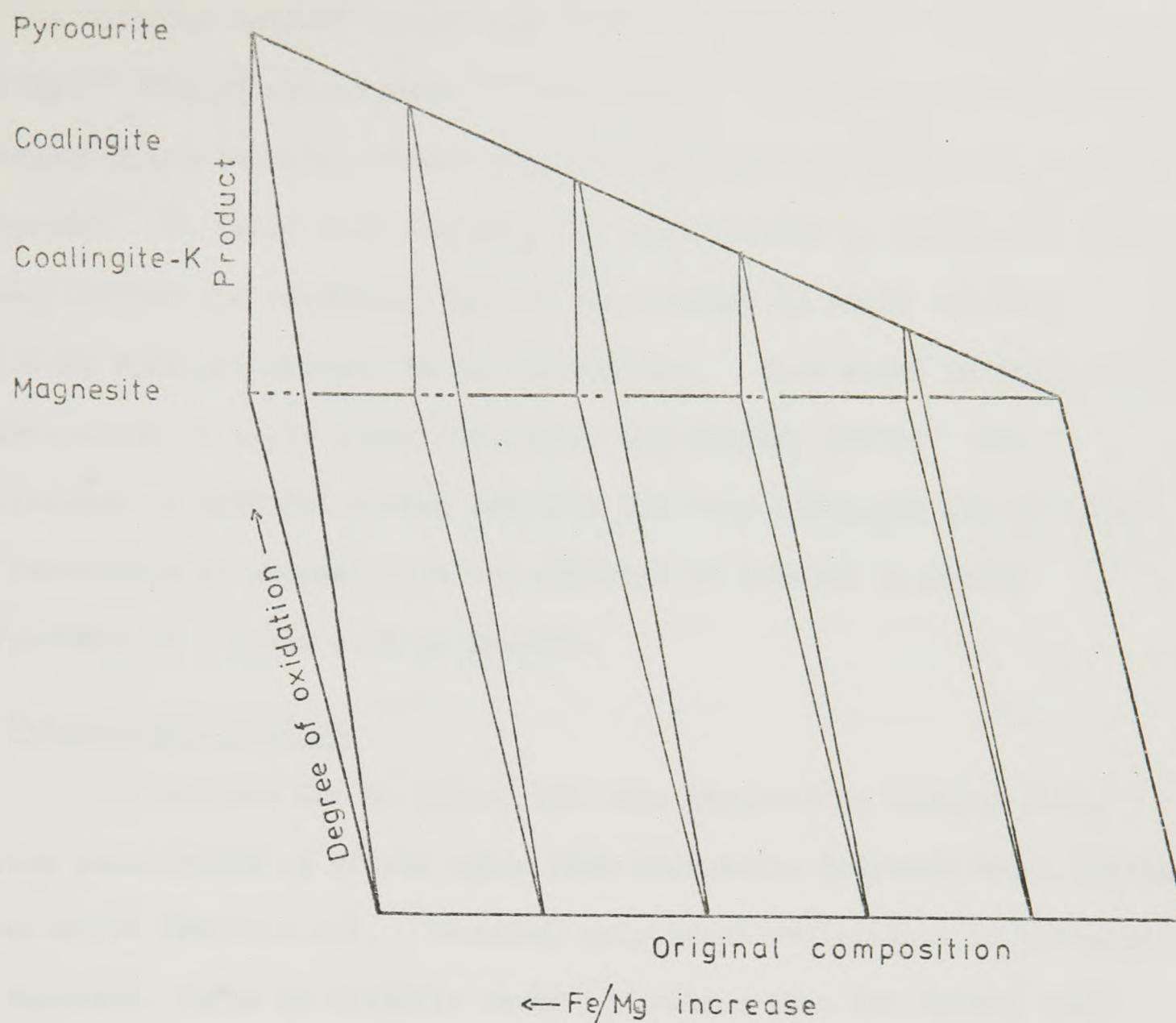


Figure 5.3. Diagram to illustrate the relationship between original composition of Fe-brucite, degree of secondary oxidation and the hydroxycarbonate mineral produced in the secondary alteration of Fe-brucite. See text for discussion.

Earley (1958) reported anomalously high chlorine values in serpentinised dunite from Lake Abitibi, Ontario and Steuber et al (1968) demonstrated that the chlorine content of dunites apparently increases on serpentinisation. Rucklidge (1972a,b) investigated in some detail the distribution of chlorine in serpentinites from the Dumont serpentinite, Quebec, using the electron microprobe. He found that chlorine was concentrated in serpentine veins cutting olivine and concluded that it was present in solid solution (replacing hydroxyl groups) in the serpentine. This seems unlikely from considerations of ionic radii (Whittaker and Muntus, 1970). The distribution of chlorine within veinlets was very irregular and it seems more reasonable to suppose that the chlorine is located in minute intergrowths of a phase such as iowaite.

5.3 Present observations

Reflections due to pyroaurite were observed on several x-ray rotation photographs of fibres taken from chrysotile asbestos veins cutting serpentinites from Shabani. Usually, only basal reflections of pyroaurite were apparent, lying at slightly lower θ values than the strong basal reflections of chrysotile at 7.3 and $3.6\text{\AA}$. However, one of the fibres examined contained sufficient pyroaurite to give a fairly full, observable diffraction pattern.

In the rotation photograph of this fibre, reflections due to pyroaurite were somewhat diffuse, and spread along Debye arcs. The orientation of the pyroaurite was determined stereographically (see chapter two section 2.3.2.1), and found to be such that an a-axis was approximately (within a few degrees) parallel to the fibre axis. This accords with the measured layer line spacing, which indicated a fibre repeat of $\sim 6.2\text{\AA}$ ($a = 3.1\text{\AA}$). Such an orientation would seem to fit in well with derivation of the pyroaurite from fibrous brucite, in the commonly observed orientation with its a-axis ($a = 3.14\text{\AA}$) parallel to the fibre axis. The transformation of brucite to pyroaurite in these respective orientations would require a minimum or reorganisation of the brucite structure.

Material thought to be pyroaurite was also observed during examination of thin sections of Shabani asbestos-bearing serpentinites. It occurred as a pale, though bright, yellow rim around prismatic crystals of magnesite, which were intergrown with chrysotile asbestos. This observation lends support to the hypothesis that a sequence of "hydroxycarbonate" minerals may be formed in response to increasingly oxidising conditions - perhaps encountered as successively nearer-surface environments are entered (see section 5.2). It is suggested that, in the present instance, magnesite (with some siderite in solid solution) was formed by the alteration of iron-bearing brucite and/or serpentine, under conditions of very low PO_2 . Subsequently, in response to more oxidising conditions, the magnesite was partially altered to pyroaurite.

The structural relationships between the magnesite, pyroaurite, chrysotile and magnetite in these fibrous intergrowths have not been fully determined. However, from optical observations it can be asserted that the c-axis of the magnesite is not parallel to the direction of elongation. Further information was provided by examination of an x-ray oscillation photograph of a similar prismatic crystal of magnesite, taken from a Shabani asbestos sample (photograph number G394, Whittaker, personal communication) - see chapter two, section 2.3.2.1.

This photograph indicated that the axis $\overline{041}$ * was parallel to the prism length. Neither the significance of this particular orientation, nor the orientation of the pyroaurite overgrowths are known. The structural orientation of magnetite, which was observed in some specimens as fibrous intergrowths is discussed in chapter six.

Coalingite-K (Mumpton et al, 1965) was detected in a slip-fibre vein of brucite, in a sample from the Jeffrey mine, Quebec (AG67.761). The coalingite-K occurred as small, red-brown masses, closely intergrown with, and apparently replacing, fibrous Fe-brucite. Unlike the material described

* referred to ortho-hexagonal axes.

by Mumpton et al (1965) the coalingite-K in the present sample was not platy in habit, although a single good cleavage gave rise to tabular fragments when material was removed by hand-picking, from surrounding vein material. Cleavage surfaces exhibited a resinous lustre. The material was oriented such that this prominent cleavage direction lay perpendicular to the fibre direction of the intergrown brucite. This somewhat unexpected orientation is discussed below.

X-ray powder patterns showed a good match with the powder data for coalingite-K given by Mumpton et al (1965, p.1896), in respect of both intensities and spacings. In most photographs the basal reflections exhibited marked orientation effects, while some grains gave rise to photographs on which were reflections at approximately 7.3 and 3.6Å; these were presumably due to closely intergrown chrysotile.

Some x-ray diffraction studies of cleavage fragments, using single crystal techniques were carried out. On all photographs strong streaking of certain reflections in the c^* direction was observed, similar to that described by Pastor-Rodriguez and Taylor (1971) and indicating regions of disordered stacking of layers. In addition, reflections were often spread along Debye arcs and some were markedly diffuse.

These studies served to confirm the indication from the orientation of the cleavage planes, that the coalingite-K was oriented with its c -axis parallel to the fibre axis of the brucite. This orientation is surprising; a less unexpected orientation would have been with an a -axis (and therefore the cleavage planes) lying parallel to the fibre axis of brucite. This orientation would permit the parallel arrangement of the layers in the brucite and coalingite-K structures, much as was the case in the pyroaurite/chrysotile intergrowths described above.

The reason for the observed orientation of coalingite-K in this vein sample is not known. A possible explanation, for which there is, however, no direct evidence, is that the coalingite-K was produced by the alteration of brucite which consisted of stacks of platelets, each oriented perpendicular to the fibre axis, rather than by the alteration of brucite consisting of laths arranged parallel to the fibre axis (see chapter four). A similar stacking of platelets to produce an apparently fibrous morphology was demonstrated for lizardite by Wicks (1969).

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CHAPTER SIX

Some observations on magnetite occurring in serpentinites from Canada and Rhodesia

The reliable recognition and interpretation of the various magnetite/serpentine textures, developed during the progressive serpentinisation of an ultramafic rock, are of relevance to the discussion of the processes involved in the production of serpentinites, particularly to isotope fractionation studies, such as that of Wenner and Taylor (1971) - discussed below, in chapter seven. Some observations on magnetite occurring in several textures in serpentinites from the Jeffrey mine, Quebec and Shabani, Rhodesia will be presented in this chapter.

6.1 Introduction

Magnetite, Fe_3O_4 belongs to the spinel group of minerals with a general formula $\text{R}_8^{\text{II}} \text{R}_{16}^{\text{III}} \text{O}_{32}$. The structural features of this group have been reviewed by Deer et al (1962) and only brief mention is therefore made here of the structure of magnetite. The spinels are cubic and are made up of planes of close packed oxygens, lying parallel to $\{111\}$ and between these, planes of cations in tetrahedral co-ordination (A positions) and in octahedral co-ordination (B positions). Structurally the spinels can be divided into two groups, termed normal and inverse. This division is made on the basis of the distribution of divalent and trivalent cations between the A and B positions, as follows -

	<u>A posn.</u>	<u>B. posn.</u>
Normal	8 R^{II}	16 R^{III}
Inverse	8 R^{III}	8 R^{II} + 8 R^{III}

Magnetite possesses the inverse spinel structure, $\text{Fe}^{\text{II}}(\text{Fe}^{\text{I}}\text{Fe}^{\text{III}})\text{O}_4$.

Chemically, magnetite is extremely variable, with a wide range of possible cation substitutions for both Fe^{II} and Fe^{III}. In igneous rocks magnetite is commonly rich in Ti (e.g. Vincent and Phillips, 1954) and associated with ulvospinel and ilmenite. Such assemblages have been found to be useful, in conjunction with experimental investigations, to the development of a geothermometer (see Buddington, Fahey and Vlisidris; 1955; Buddington and Lindsley, 1964).

From the published literature it seems that little attention has been paid to the chemistry of magnetite occurring in serpentinites. There have been several published accounts of studies of the alteration of primary igneous spinels (now as relict grains in serpentinite) to more iron-rich composition some of which approach the magnetite end-member. For example the work of Lapham (1964), Engin and Aucott (1971) and Golding and Bayliss (1968).

Some mention will be made of magnetite associated with chromite but the greater part of the discussion will be confined to magnetite thought to have been produced as a result of the liberation of iron from silicate minerals, during serpentinisation.

Magnetite associated with serpentinites may contain fairly appreciable quantities of chromium - in excess of 15% Cr₂O₃ (Wenner and Taylor, 1971 and section 6.3.2). Morgan, Lally and Holmes (1973) reported that small amounts of chromium and cobalt were associated with the "contaminating minerals such as chromite and magnetite" in asbestos samples from Rhodesia and Canada,* while Fawley (1959) reported magnetite containing 8% nickel, from a Tanganyikan serpentinite (see Deer et al, 1962). Nickel is often sufficiently abundant in serpentinites (not necessarily in the magnetite) to be economically significant - for instance in the serpentinites of the Manitoba Nickel Belt (Coats, 1968).

* The samples used by Morgan et al were the standard, chrysotile reference samples of the International Union against Cancer. These consist of material from a single Rhodesian mine (sample A) and blended material from eight Canadian mines (sample B).

6.2 Review of previous studies

As a general observation, it can be stated that the extent of magnetite production during the serpentinisation of the primary, essentially anhydrous rock depends to a considerable degree upon the compositions of the olivines and pyroxenes. As an extreme example, the highly forsteritic olivines of metamorphosed dolomites do not give rise to magnetite, whereas the more fayalitic olivines of layered intrusions and alpine-type ultramafic rocks* may give rise to considerable quantities of magnetite on serpentinisation.

The degree to which the ferrous iron, occurring in the primary silicate minerals of the ultramafic rock is oxidised during serpentinisation is also important. Iron released by the dissolution of olivine and pyroxene can only produce magnetite if sufficient Fe^{III} is available; otherwise it is likely to be incorporated into brucite.**

The apparent mobility of magnetite during progressive serpentinisation was commented on by Wicks (1969). During examination of serpentinite samples which came from a variety of localities and which exhibited different degrees of serpentinisation, Wicks noted a somewhat ill-defined sequence of magnetite textural types, as follows:

1. Occurrence in mesh texture serpentine
 - a. at the lizardite-olivine interface
 - b. in the mesh centres.
2. Migration out of mesh textures
 - a. along the central parting of mesh rims, and relict grain boundaries and interstices.
 - b. as lenses and dendritic aggregates (1 - 5 mm)
 - c. in veins and shear zones.

* see for example Thayer (1967) for a resume of the characteristics of alpine-type ultramafic rocks.

** Greenalite, $\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_4$ the iron-end member of the septeclorites is of very restricted occurrence and is not an important iron-bearing phase in serpentinites.

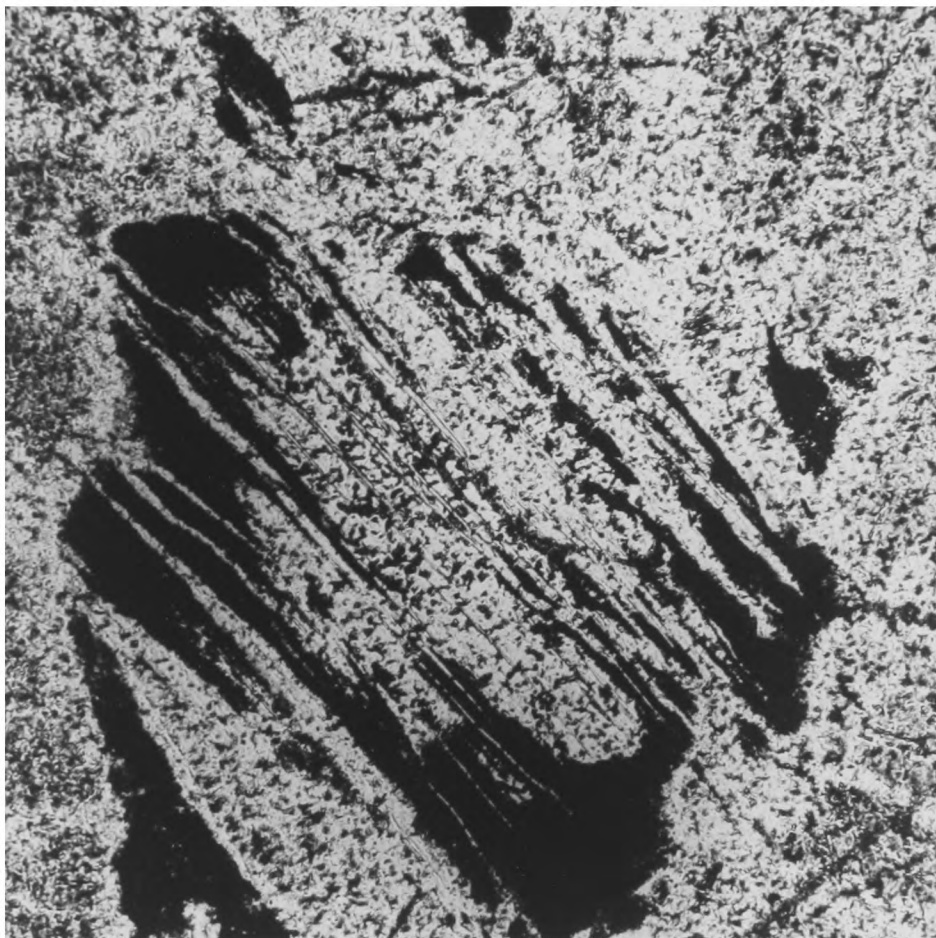


Figure 6.1. Pyroxene bastites rimmed and veined by magnetite. Specimen AG 67.780. Plane polarised light; magnification x10.

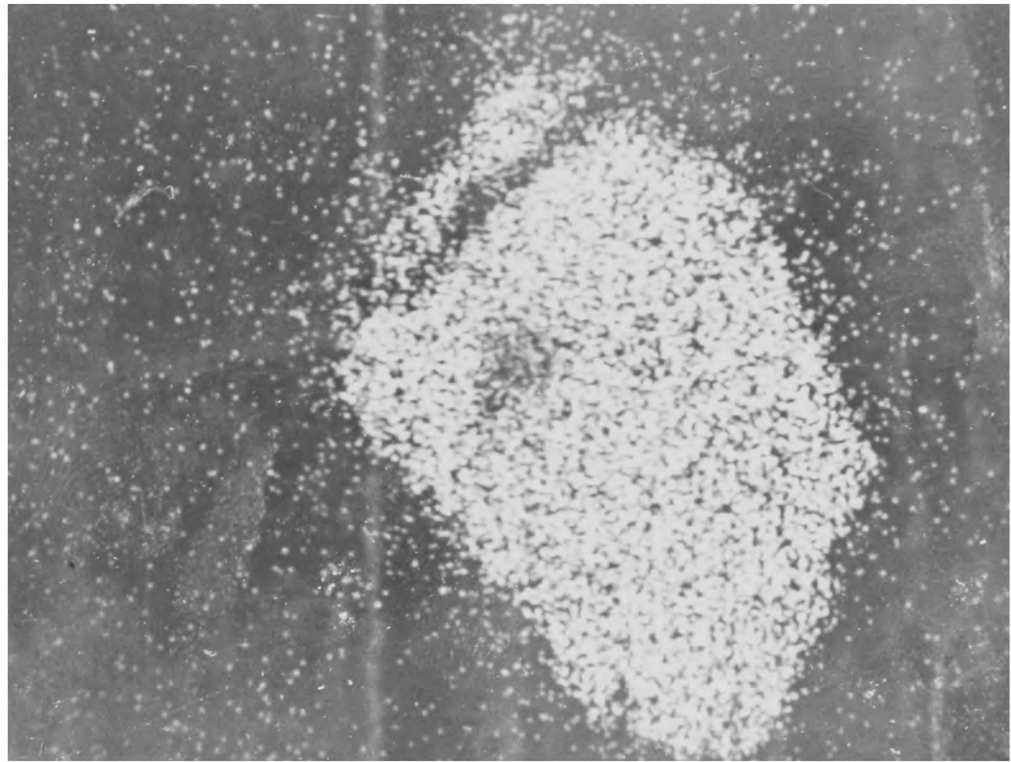
Wicks suggested that there might be some correlation between the extent of migration of magnetite, and the increasing chemical homogeneity of lizardite in the mesh texture units (indicated by his microprobe investigations) as serpentinisation progressed.

Il'vitsky and Romanenko (1965) also recognised several generations of magnetite, developed during the hydrothermal alteration (especially serpentinisation) of ultrabasic rocks. They considered that these several generations could be correlated with different stages of metamorphism. Their divisions are broadly similar to those given by Wicks and are given below:

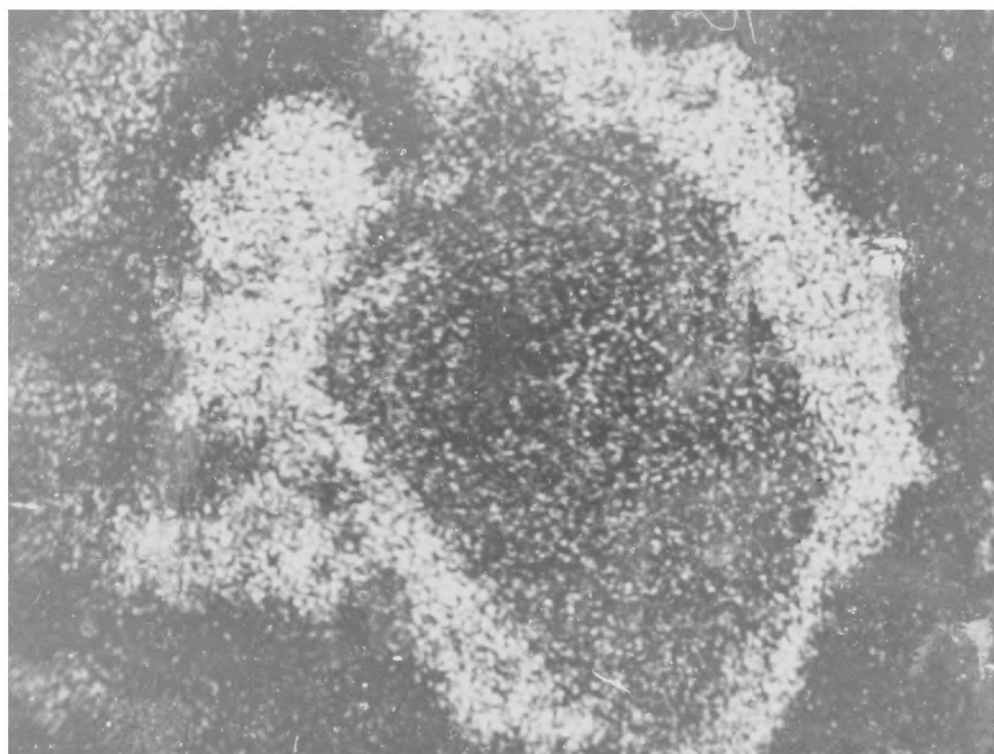
1. "magmatic" magnetite developed from chrome-spinel as isolated crystals and grains.
2. mesh texture magnetite formed during serpentinisation, as intersecting stringers.
3. "heaped dust-like masses formed in serpentinite during the chrysotilisation of pyroxene or olivine".
4. segregations of "columnar magnetite" in stringers associated with chrysotile, 'serpophite' or carbonate
5. microgranular stringers and dusty disseminations of magnetite ± sulphides.

They consider that stages 1 to 4 are characteristic of both chrysotile and antigoritic serpentinites, while stage 5 predominates in the "recrystallised (antigoritic) serpentinite".

Shteynberg and Malakhov (1965) discussed the behaviour of iron during serpentinisation and concluded that magnetite is frequently formed during the recrystallisation of serpentinites, rather than during serpentinisation. In disputing a suggestion attributed to Sobolev that the degree of oxidation of iron could be estimated from the amount of secondary (i.e, not igneous) magnetite and used as an index of the degree of serpentinisation, they claimed that even under conditions of fairly extensive serpentinisation most of the iron might still be unoxidised, and located in the serpentine minerals.



(a)



(b)

Figure 6.2. X-ray back scatter images from a chromite grain rimmed by magnetite. Specimen AG 67.992.

a) Distribution of Cr

b) distribution of Fe

Keith and Bain (1932) observed needles of magnetite in asbestos veins and concluded from textural evidence that the magnetite was precipitated after the chrysotile fibres. Van Biljon (1960) also reported minute needles of magnetite lying parallel to the fibres in chrysotile asbestos from Havelock, Swaziland.

6.3 Present observations and interpretation

6.3.1 Petrographic examination

The samples examined during the present studies came from highly serpentinised, asbestos-bearing rocks. In these specimens magnetite commonly occurs in veins associated with brucite and/or chrysotile, as well as in the massive, host serpentinite.

In rocks from the Jeffrey mine, Quebec well developed pyroxene-bastites (lizardite) are common, sometimes with relict clinopyroxene lamellae. Associated with these bastites is abundant magnetite, occurring as rims following the relict grain boundaries (apparently) and as lamellae running almost parallel to the relict pyroxene, cleavage traces (see figure 6.1). Very little magnetite is, however, associated with textures thought to be derived initially, from the serpentinisation of olivine grains (mesh texture serpentine).

This association of abundant magnetite with pyroxene-bastites is rather surprising. Usually the serpentinisation of pyroxene occurs with the production of little or no magnetite (Wicks, 1969 p. 411). The scarcity of magnetite in the somewhat altered mesh texture serpentine is in accord with the sequence of magnetite migration suggested by Wicks (stage 2c).

Magnetite is also associated with chromite grains in the Jeffrey mine samples; it occurs as narrow rims of relatively pure magnetite (see figure 6.2), apparent in reflected light as a rim of white material surrounding slightly grey chromite. In thin section the chromite is just translucent and deep red-brown in colour. The boundary between magnetite and chromite is apparently sharp.

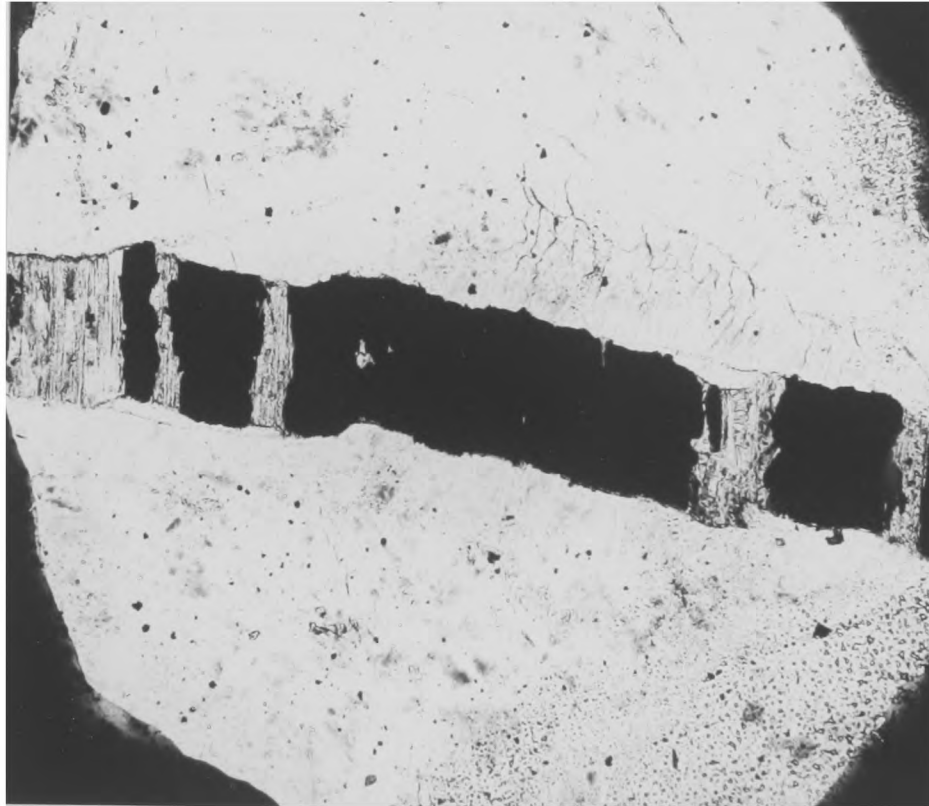


Figure 6.3. Magnetite of prismatic habit, intergrown with fibrous brucite in a cross-fibre vein cutting sample AG 67.780. Plane polarised light; magnification x10.

Brucite/magnetite veins - both cross-fibre and slip-fibre - are common in the Jeffrey mine samples and in these the magnetite is frequently columnar to fibrous in habit, and closely intergrown with brucite, as illustrated by figure 6.3.

In the Shabani serpentinites, magnetite is again widespread and is noticeable in the host rock of hand specimens as small irregular clusters of grains. In thin section the textural development of magnetite in the host rock can be broadly divided into three categories (see figure 6.4). Of these one can be correlated with the clusters visible in hand specimen, which are seen to consist of aggregates of subhedral grains, which seem to bear little relation to the serpentine textures. A second textural type consists of thin veinlets of magnetite often surrounding hourglass textures (probably mainly antigorite). Magnetite intergrown with carbonate, which appears to be replacing serpentine and which was shown, by x-ray powder photographs to be magnesite, constitutes a third textural variety. In these carbonate textures a notable feature is the frequent development of numerous sub-parallel, elongate 'pencils' of magnetite.

The Shabani specimens are cut by veins of long, cross-fibre chrysotile asbestos, usually with a prominent central parting occupied by massive magnetite. In thin section magnesite can frequently be observed, intergrown with vein chrysotile, as elongate, prismatic crystals (see chapter five).

Magnetite occurs in the chrysotile veins as fine, intimately intergrown fibres (figure 6.5). These magnetite fibres may grow out continuously from the massive material of the central parting or be apparently isolated, within vein chrysotile. Observation of polished specimens in a reflected light microscope revealed the presence of occasional grains, thought to be chromite, within the massive magnetite of the central vein parting.

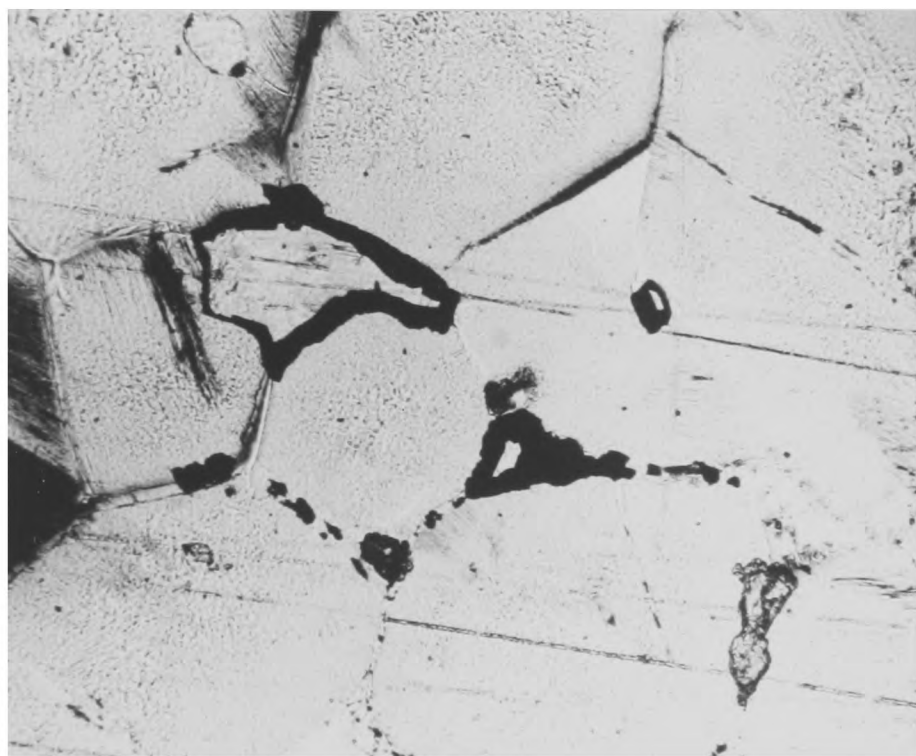
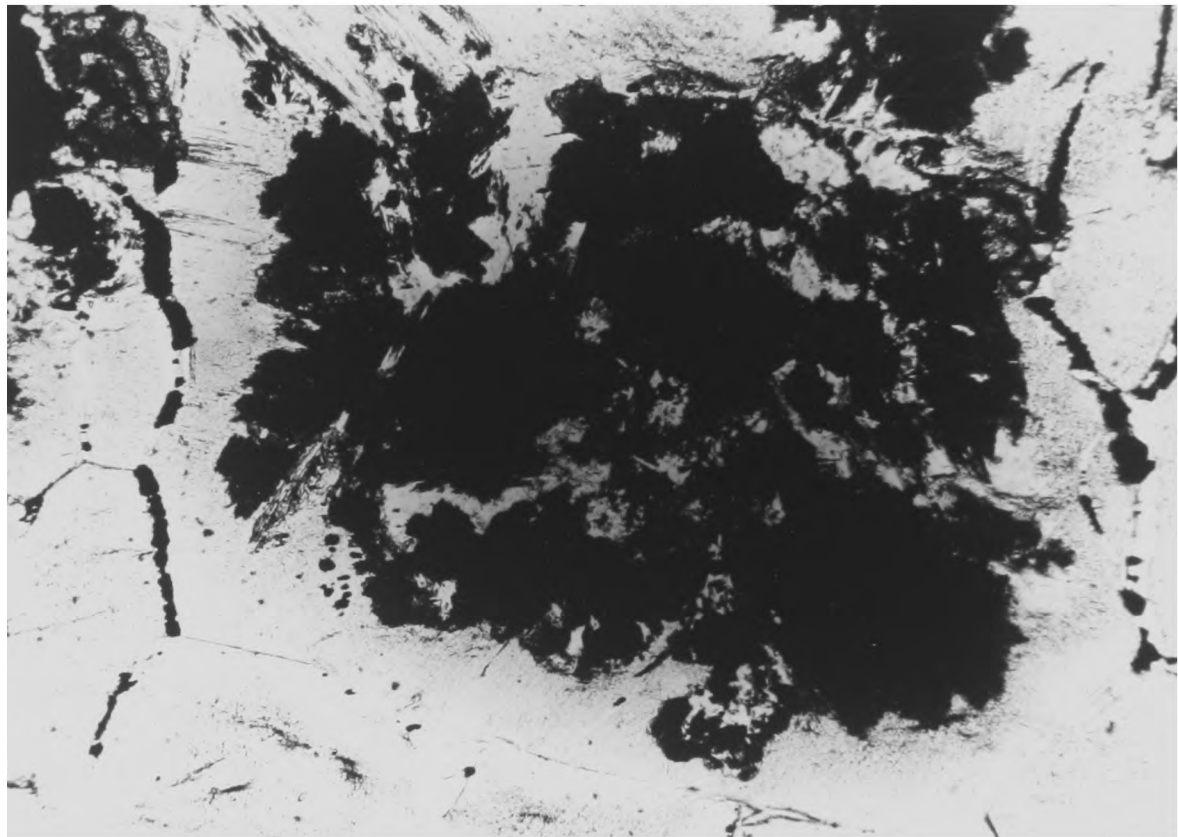


Figure 6.4. Some representative magnetite textural types from the Shabani serpentinites.

- a) cluster of subhedral grains; plane polarised light
magnification x10: sample B.14.
- b) thin veinlets rimming serpentine textural units;
plane polarised light; magnification x15: sample B.14.

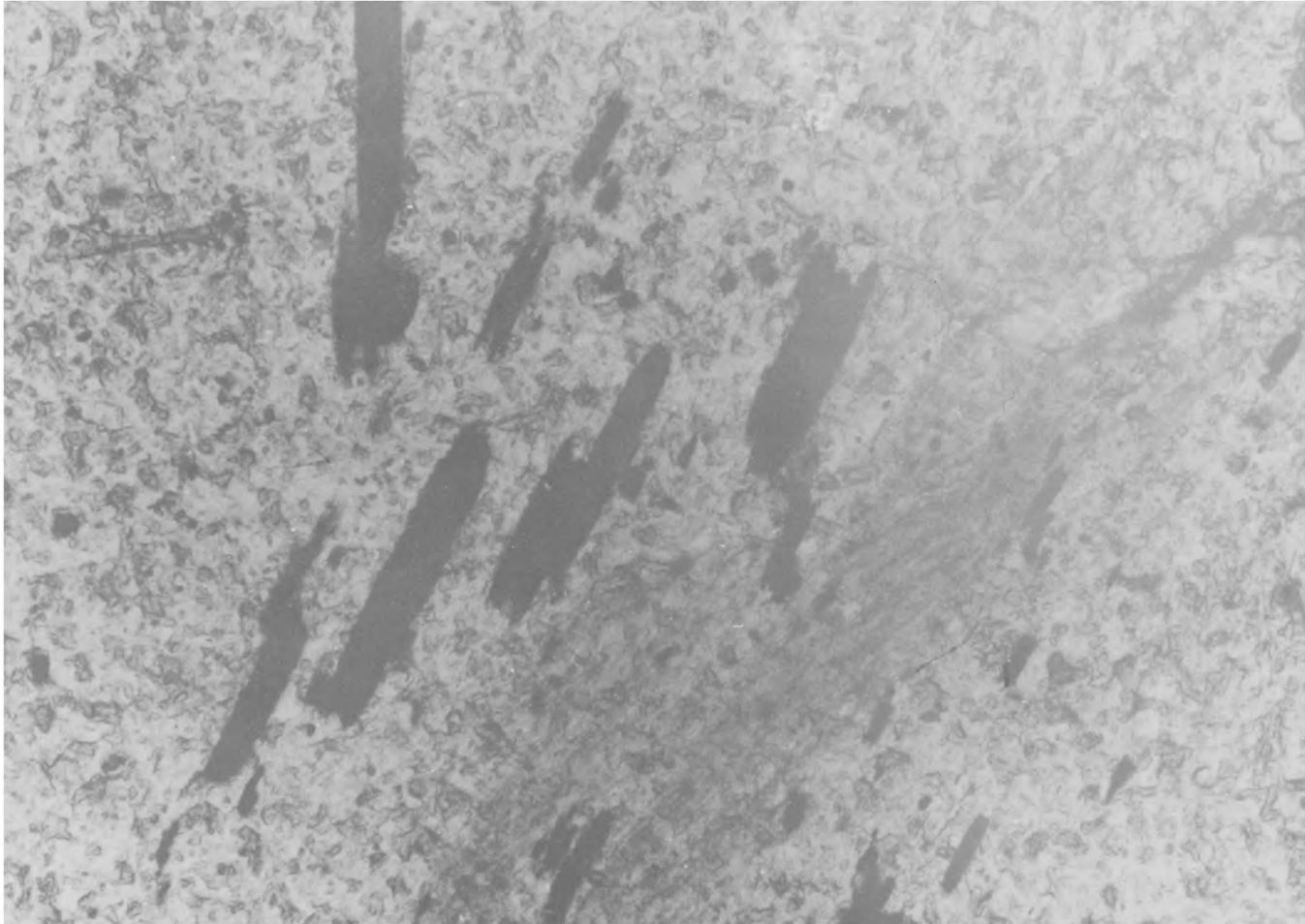


Figure 6.4 continued.

c) oriented pencils of magnetite; plane polarised light;
magnification x40; sample B.23. Note the different
alignment of the pencil in the top left hand corner.

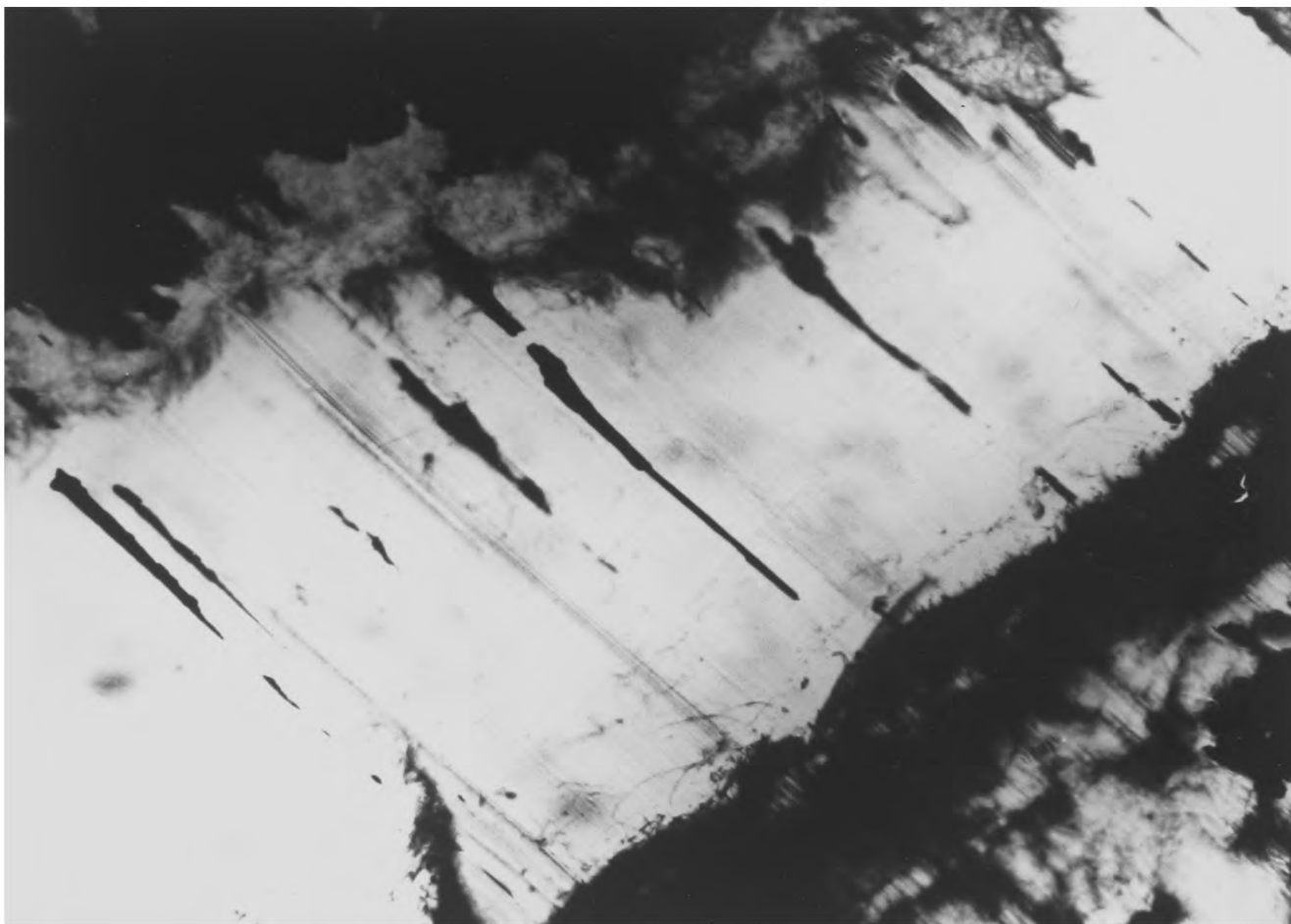
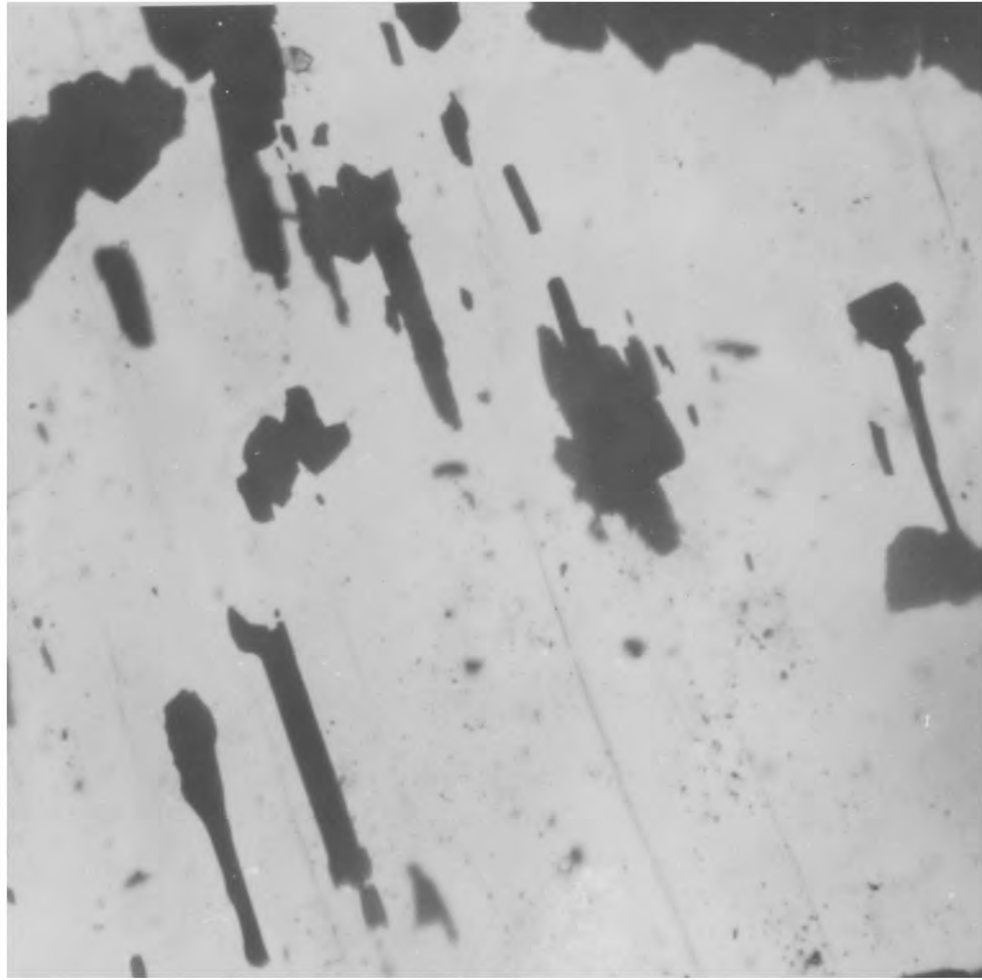


Figure 6.5. Fibrous magnetite intergrown with chrysotile asbestos.
Plane polarised light; magnification x40; specimen B.14.

6.3.2 The chemical composition of magnetite in some of the textures

Preliminary chemical data were obtained on magnetite occurring in the Shabani serpentinites by optical emission spectrography, performed on a Hilger-Watts medium length spectrograph. The magnetite samples were taken so far as possible, from three distinct textural types, as follows:

- (1) clusters of magnetite in the wall rock.
- (2) massive magnetite in the central parting of the chrysotile asbestos veins
- (3) fibrous magnetite intergrown with the vein chrysotile.

The non-magnetic impurities were separated from the magnetite after crushing the samples, under acetone in an agate mortar. The powder was shaken up, under acetone in a glass beaker and, with the aid of a small hand magnet the non-magnetic material only was poured off. This process was repeated until an apparently 'clean' sample (when viewed under a binocular microscope) was obtained. In some cases the fine scale of the intergrowths prevented the achievement of a good separation.

The mineralogical purity of the separations was checked from x-ray powder photographs, which were also used for a survey of cell edge dimensions (see below). The data obtained from the optical spectrography were interpreted in a semi quantitative fashion and indicated the presence of minor Cr, Ni and Mn together with trace Co and V. Mg and Si were also detected but it is thought that these represent in the main, serpentine contamination. The data are not sufficiently precise to permit any distinctions to be drawn between different textural types but provide a general indication of the chemistry of the magnetite occurring in the Shabani serpentinites.

TABLE 6.1

Cell edge values of some spinels

<u>Name</u>	<u>Formula</u>	<u>a(Å)*</u>	<u>Δa**</u>
Magnetite	$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$	8.396	-
Magnesioferrite	$\text{MgFe}^{\text{III}}_2\text{O}_4$	8.383	-0.0013
Franklinite	$\text{ZnFe}^{\text{III}}_2\text{O}_4$	8.420	+0.0024
Jacobsite	$\text{MnFe}^{\text{III}}_2\text{O}_4$	8.51	+0.0114
Trevorite	$\text{NiFe}^{\text{III}}_2\text{O}_4$	8.43	+0.0034
Chromite	$\text{Fe}^{\text{II}}\text{Cr}_2\text{O}_4$	8.378	-0.0018
Ulvospinel	$\text{Fe}^{\text{II}}\text{TiO}_4$	8.53	+0.0134

* From Deer et al (1962)

** Change in cell edge associated with 10% substitution of magnetite by the end-member composition (assuming linear variation).

The various members of the spinel group can be characterised by the cell edge dimension, a (Table 6.1). A formula relating the value of a to particular compositions was developed by Mikheev (1955) - see Deer et al, 1962. The application of this formula, however, requires a knowledge of the substituting cations and their ionic radii.

In the light of the data from optical spectrography and from a consideration of the published chemical data on magnetite occurring in serpentinites, it seems that the most commonly substituting elements are Ni and Cr, and to a lesser extent Mn, Co and V. It was thought that Mg might also be of interest in view of the Mg rich nature of serpentinites and the existence of natural spinels approaching the composition of the magnesio ferrite end-member, MgFe_2O_4 .

If it is assumed that there is a linear variation in a with composition, between the several end-member/magnetite pairs of interest then the "rates of change" of a with composition, given in Table 6.1 can be calculated. The variety of possible substitutions for iron and the opposing effects of some of these cations (particularly of Ni^{2+} and Cr^{3+}) on the cell edge dimension means that interpretation of cell edge data in terms of composition cannot be unambiguous.

Despite this obvious difficulty it was nevertheless thought worthwhile to carry out a survey of cell edge values of the available magnetite powder samples from the Shabani serpentinites and of magnetite hand-picked from Jeffrey mine specimens. It was hoped that such a survey, in conjunction with the spectrographic information and limited microprobe investigation (see below), might indicate a convenient "finger-print" method for the characterisation of chemically different generations of magnetite.

Cell edge values were determined from the measurements of the positions of reflections on powder films, made using a Hilger-Watts film measuring rule. The films were taken in 57.3 mm radius powder cameras in

TABLE 6.2

Cell edge values of some magnetite samples, determined from
measurement of powder photographs

<u>Sample No.</u>	<u>Locality</u>	<u>Textural type</u>	<u>a (Å)</u>
B.18	Shabani, Rhodesia	CP	8.395
B.18	Shabani, Rhodesia	CP	8.395
B.18	Shabani, Rhodesia	F	8.394
B.18	Shabani, Rhodesia	W	8.394
G.20	Shabani, Rhodesia	CP	8.395
G.20	Shabani, Rhodesia	CP	8.396
I.5	Shabani, Rhodesia	CP	8.395
AG67-1044	Jeffrey mine, Quebec	V	8.396
AG67-761	Jeffrey mine, Quebec	V	8.396
AG67-780	Jeffrey mine, Quebec	W	8.395
SEP 5 (a)	Bell mine, Quebec	1	8.395
SEP 5 (a)	Bell mine, Quebec	2	8.394
SEP 11	Black Lake, Quebec	1	8.396
SEP 1	Havelock, Swaziland	2	8.392
SEP 2	Havelock, Swaziland	2	8.392

Key to textural types -

CP - massive magnetite in central parting of asbestos veins

F - fibrous magnetite, intergrown with asbestos

W - magnetite concentrated from wall rock

1 - fibrous magnetite, picked from concentrate

2 - granular magnetite, picked from concentrate

which the Straumanis film setting was used, permitting a straightforward correction for film shrinkage to be made. Filtered iron or cobalt radiation was used. The cell edge values corresponding to the d-spacings calculated for each reflection were plotted against the extrapolation function:

$$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

due to Nelson and Riley (see for instance Nuffield, 1966). The best fit straight line through these points was calculated, using the method of least squares and this line extrapolated to the zero of the function (i.e. to $\theta = 90^\circ$). Some selection of the more reliable reflections and subsequent re-measurement was carried out. The values of a finally obtained are given in Table 6.2.

As can be seen from this table the measured values of a all fall near to the value of $8.3963 \pm 0.0005 \text{ \AA}$ given by Basta (1957) for essentially pure magnetite from Bisperg, Sweden. A value of $a = 8.396 \text{ \AA}$ is given for magnetite by Deer et al (1962). The values of a for magnetite from the three textural types investigated do not differ significantly.

Since most of the cell edge values are slightly ($\sim 2\%$) less than that for pure magnetite it is possible to infer that Ni substitution in the magnetite of the serpentinites studied is probably slight and not particularly variable between different textural types. The general diminution in a is thought to be due to substitution for Fe^{+++} by Cr^{+++} (although possibly in part to Mg^{++} substitution for Fe^{++}).

The cell edge values of some magnetite samples which were kindly provided by Turner Brothers Asbestos Co., and which had been separated from commercial asbestos samples, were also determined. Samples from the Bell and Black lake deposits (Canada) gave values similar to those obtained for magnetite from the Shabani and Jeffrey mine serpentinites but the values for two samples from Havelock, Swaziland are significantly lower, perhaps

TABLE 6.3

Electron microprobe analyses of magnetite from several textural settings*

	1	2	3	4
FeO	30.25	30.12	29.30	28.98
MgO	0.58	1.14	1.18	1.21
NiO	1.62	1.48	1.56	1.75
MnO	0.13	0.15	0.27	0.29
Fe ₂ O ₃	67.22	66.95	65.12	64.41
TiO ₂	0.02	0.00	0.00	0.01
Al ₂ O ₃	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.18	0.16	2.57	3.35
SiO ₂	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00

Numbers of ions on the basis of 32(0)

Fe ^{II}	7.806	7.753	7.517	7.430
Mg	0.267	0.523	0.540	0.553
Ni	0.402	0.366	0.385	0.432
Mn	0.034	0.039	0.070	0.075
Fe ^{III}	15.611	15.507	15.035	14.859
Ti	0.005	0.000	0.000	0.002
Al	0.000	0.000	0.000	0.000
Cr	0.044	0.039	0.623	0.812
Si	0.000	0.000	0.000	0.000

- 1 aggregate of anhedral magnetite grains wall rock
- 2 aggregate of subhedral magnetite grains, wall rock
- 3 rim of magnetite on serpentine texture, wall rock
- 4 rim of magnetite on serpentine texture, wall rock
- 5 rim of magnetite on serpentine texture, wall rock

* Sample B-14 from Shabani, Rhodesia.

TABLE 6.3 (Contd.)

	5	6	7
FeO	28.05	29.62	29.76
MgO	1.96	0.88	1.01
NiO	1.81	1.78	1.42
MnO	0.24	0.19	0.19
Fe ₂ O ₃	62.34	65.83	66.15
TiO ₂	0.01	0.01	0.02
Al ₂ O ₃	0.04	0.04	0.00
Cr ₂ O ₃	5.55	1.65	1.45
SiO ₂	0.00	0.00	0.00
Totals	100.00	100.00	100.00

Fe ^{II}	7.143	8.538	7.621	8.515	7.650	8.514
Mg	0.890		0.404		0.463	
Ni	0.443		0.440		0.351	
Mn	0.062		0.050		0.050	
Fe ^{III}	14.288	15.640	15.238	15.656	15.300	15.657
Ti	0.002		0.002		0.005	
Al	0.014		0.015		0.000	
Cr	1.336		0.401		0.352	
Si	0.000		0.000		0.000	

- 5 rim of magnetite on serpentine textures, wall rock
- 6 massive vein magnetite, asbestos vein
- 7 massive vein magnetite, asbestos vein

TABLE 6.3 (Contd.)

	8	9	10
FeO	29.67	29.64	29.97
MgO	0.91	1.20	1.09
NiO	2.09	1.09	1.30
MnO	0.19	0.29	0.18
Fe ₂ O ₃	65.96	65.90	66.62
TiO ₂	0.00	0.04	0.00
Al ₂ O ₃	0.00	0.01	0.01
Cr ₂ O ₃	1.18	1.82	0.83
SiO ₂	0.00	0.00	0.00
Totals	100.00	100.00	100.00

Fe ^{II}	7.645	8.631	7.604	8.501	7.705	8.573
Mg	0.418		0.551		0.500	
Ni	0.518		0.270		0.321	
Mn	0.050		0.076		0.047	
Fe ^{III}	15.293	15.580	15.210	15.664	15.412	15.618
Ti	0.000		0.009		0.000	
Al	0.000		0.004		0.004	
Cr	0.287		0.441		0.202	
Si	0.000		0.000		0.000	

8 massive vein magnetite, asbestos vein

9 massive vein magnetite, asbestos vein

10 fibrous magnetite, asbestos vein

Note - In the recalculation of the analyses from the original data (weight per cent metals) Fe was allocated to FeO and Fe₂O₃ so as to bring the oxide total for each analysis to 100.00%

due to a greater degree of Cr substitution.

The electron microprobe method of analysis is of obvious application to any study of serpentinite mineralogy. Unfortunately only a small number of reliable probe analyses have been obtained*. From these data (Table 6.3), which are restricted to a single Shabani specimen** it can be seen that the Ni content of all the magnetite grains analysed were fairly uniform at about 1.5 to 2% NiO (confirming the indication of the cell edge values). Manganese contents are consistently low at < 0.5% MnO. The only element which seems to be of any value in distinguishing chemically between textural varieties of magnetite is chromium.

The analyses suggest that magnetite occurring as aggregates of sub-hedral grains (analyses 1 and 2, figure 6.4a) is generally Cr-poor (< 1% Cr_2O_3), while that associated with (generally surrounding) the hourglass serpentine (analyses 3, 4 and 5 figure 6.4b) tends to be more Cr-rich, (3-5% Cr_2O_3). Vein magnetite (analyses 6 to 10 figure 6.5) seem to have Cr contents which are intermediate in value.

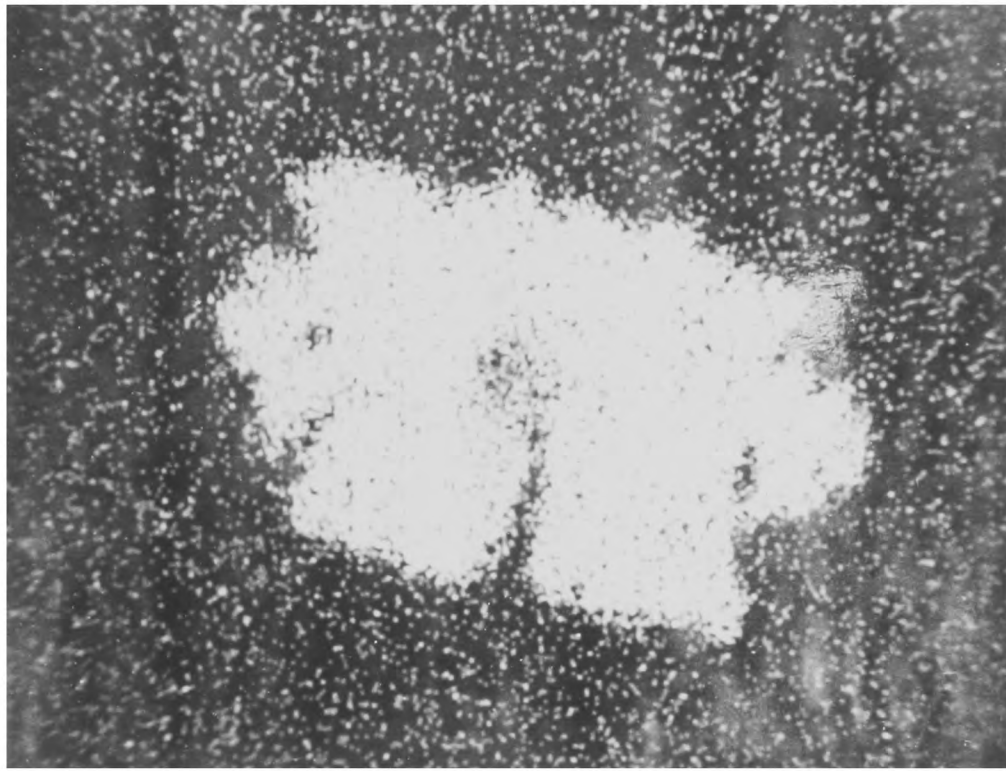
In view of the association of the 'Cr-rich' magnetite with replacement type hourglass textures (Wicks, 1969) it is suggested that such magnetite may be generated during a metamorphic event, post-dating serpentinitisation, as was noted by Wicks (1969) after a review of the literature concerning the occurrence of antigorite:

"The development of antigorite is not limited to any particular type of metamorphism but does seem to depend on the influence of an external force whether it be dynamic, thermal or regional metamorphism".

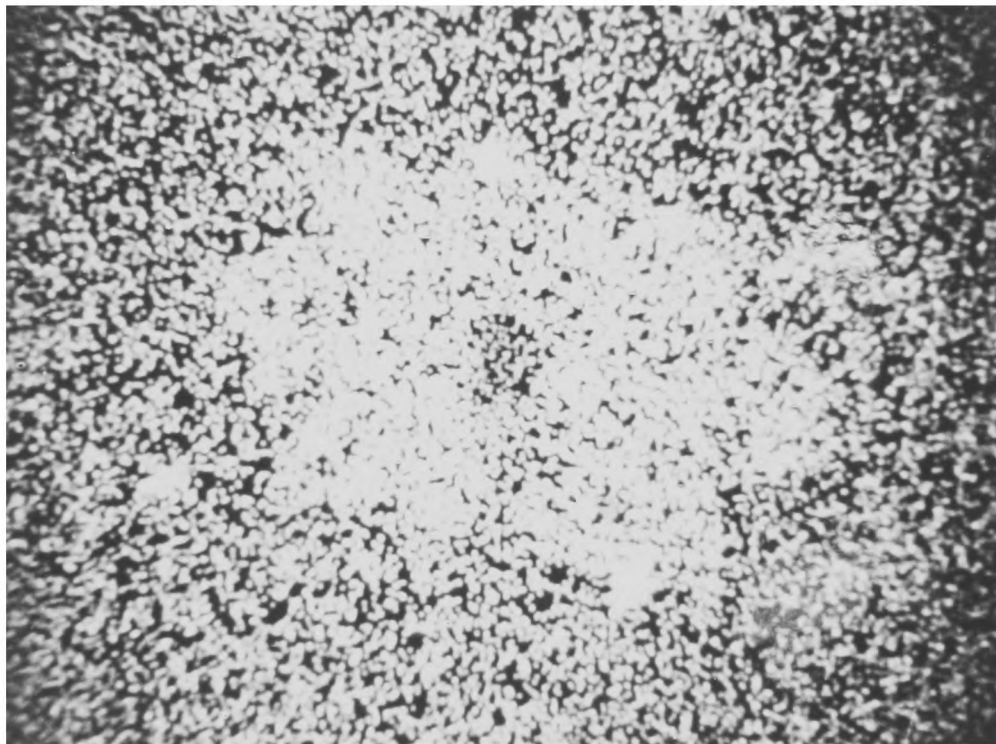
(p.422).

* performed on the Geoscan electron microprobe, Dept. of Geology, Manchester.

** Semi-quantitative confirmation of these results was obtained from observations on several other Shabani specimens, using the A.E.I. microprobe in the Department of Geology and Mineralogy, Oxford.



(a)



(b)

Figure 6.6. X-ray back scatter images from a magnetite grain occurring in a brucite vein cutting specimen AG 67.992.

a) Distribution of Fe

b) Distribution of Ni

On the other hand the association of Cr-poor magnetite with the vein chrysotile suggests that this variety of magnetite is generated during the later stages of serpentinisation and vein formation.

The microprobe investigation also served to confirm the indications from reflected light microscopy that chromite (presumably relict) occurs within the massive magnetite of the central vein parting. This observation may throw some light on the mode of formation of the chrysotile asbestos veins. Rather than having been produced entirely by some process involving the introduction of 'new' material, and consequent local expansion perpendicular to the vein walls (i.e. equivalent to the opening of a fracture and its subsequent infilling by asbestos), the veins may have been formed, at least in part by the replacement (or recrystallisation) of wall rock material. The chromite grains were not replaced during vein formation but remained in their original positions within the rock body.

Investigation of rocks from the Jeffrey mine using the Oxford microprobe demonstrated again, the generally low degree of substitution in magnetite. Nickel contents once more showed little variation between textural types, with NiO values of $\sim 1\%$. X-ray back scatter images of vein magnetites associated with brucite demonstrated the existence of small, discrete grains of nickel-rich material, (figure 6.6). These are thought likely to be heazlewoodite, Ni_3S_2 or millerite NiS , which commonly occur in serpentinites (see for instance Rucklidge, 1972). Analysis for manganese indicated uniformly low values of $\sim 0.3\%$ MnO in all textural types. X-ray back scatter images also served to confirm the optical observations of chromite, rimmed by magnetite and showed that this magnetite is Cr-bearing, (see figure 6.2).

In summary, it might be said that the most notable conclusion to be drawn from the somewhat limited data presented in this section, is the generally very low degree of substitution for iron, in the magnetite associated with the serpentinites studied; this feature does not seem to have been much

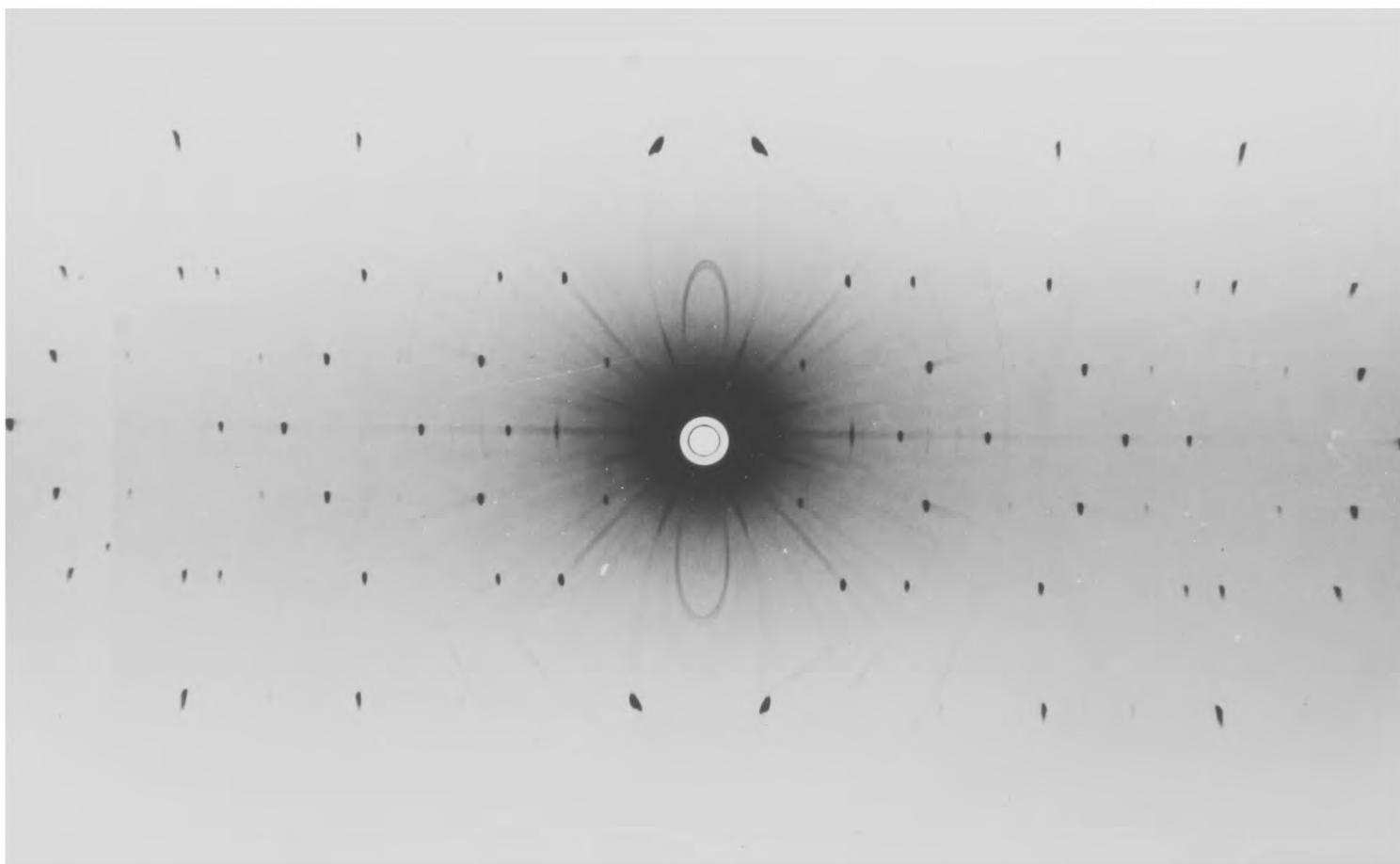


Figure 6.7. X-ray rotation photograph of fibrous magnetite taken from chrysotile asbestos vein, specimen B18. Film taken using Mn filtered Fe radiation. The layer line spacing indicates an axial repeat of $8.42 \text{ \AA}$.

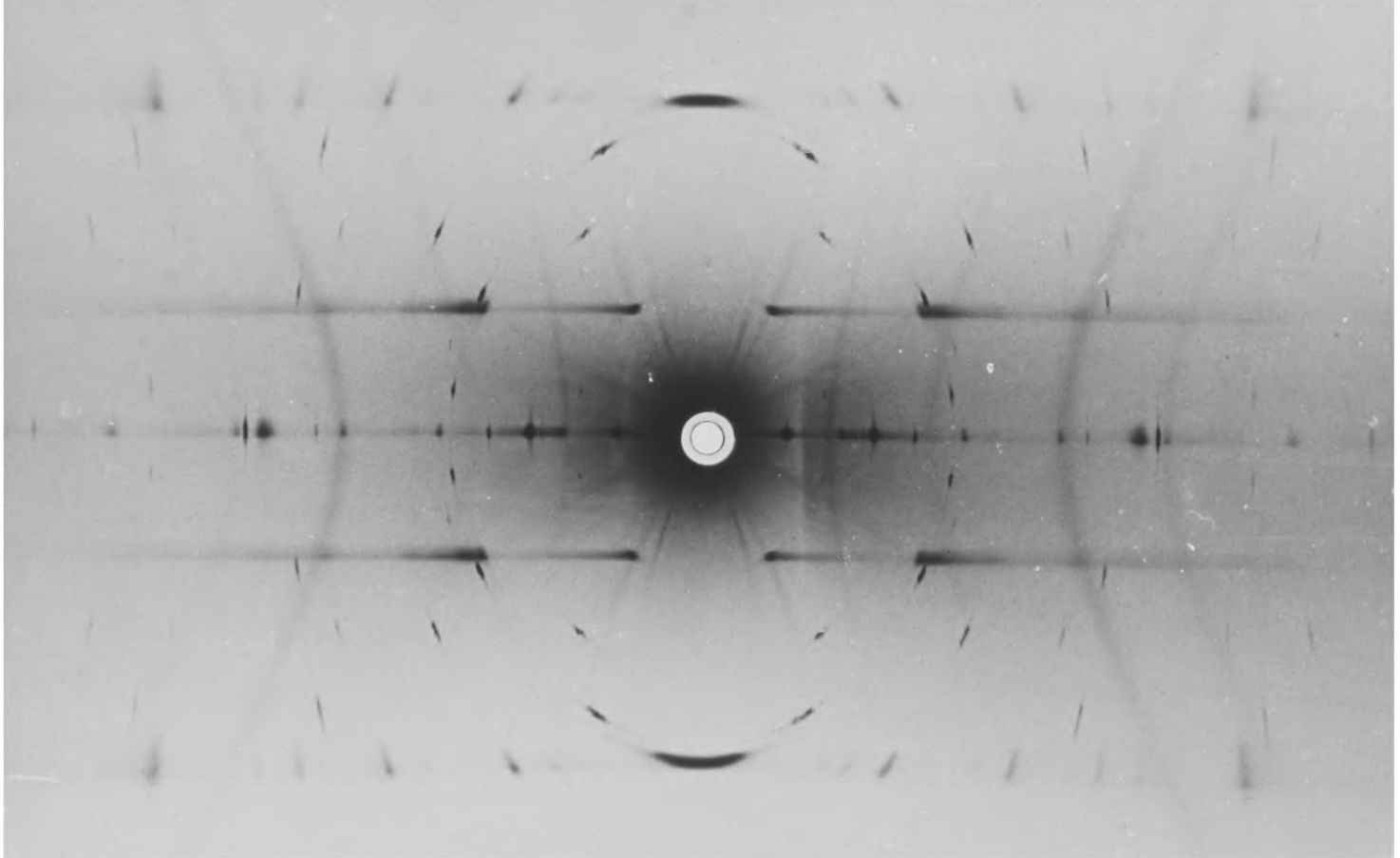


Figure 6.8. X-ray rotation photograph of fibrous magnetite taken from chrysotile asbestos vein, specimen B.14. Film taken using Mn filtered Fe radiation. The layer line spacing indicates an axial repeat of $14.53 \text{ \AA}$.

emphasised previously. Some additional discussion of Cr-bearing magnetite and its relevance to recent studies of the process of serpentinisation is undertaken in the next chapter.

6.3.3 X-ray studies of fibre texture

Several x-ray photographs were taken of fibrous magnetite/brucite intergrowths taken from veins cutting samples from Jeffrey mine, with a view to determining the relative structural orientations of the two minerals. While the brucite was usually well oriented, with an a-axis parallel to the fibre axis the magnetite showed no evidence of a preferred orientation. Rather, it gave rise to closely spaced, sharp spots lying around Debye arcs. A similar result was obtained by Donnay (1944).

X-ray rotation photographs were also taken of some of the magnetite fibres, intergrown with chrysotile in the asbestos veins of the Shabani specimens. It was found that there is sometimes a strong development of preferred orientation, as evidenced by figures 6.7 and 6.8. The zone axes lying parallel to the fibre axis were determined stereographically (see section 2.3.2.1 of chapter two). The fibre giving rise to the photograph of figure 6.7 was found to have been rotated about an axis $\langle 100 \rangle$, while the photograph of figure 6.8 indicates that an axis $\langle 111 \rangle$ was parallel to the fibre axis. In both instances the repeat period calculated for the particular axis and that indicated by the measured layer line spacing were in good agreement (see captions to figures).

The reasons underlying these particular orientations are not readily apparent, there is no obvious structural match between the sheets of hydroxyls lying parallel to $\langle 100 \rangle$ in the chrysotile fibrils and magnetite in either of the observed orientations. Neither is there any apparent fit of the magnetite structure with pyroaurite in the orientation reported above in chapter five (with an a-axis parallel to the fibre axis). A less surprising orientation would have been with the planes of close-packed oxygens of magnetite (lying parallel to the faces of $\langle 111 \rangle$) arranged parallel to the basal planes of hydroxyls in chrysotile or in pyroaurite; with an axis such as $\langle 110 \rangle$ parallel to the fibre axis.

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Several x-ray photographs were taken of fibrous magnetite/brucite intergrowths taken from veins cutting samples from Jeffrey mine, with a view to determining the relative structural orientations of the two minerals. While the brucite was usually well oriented, with an a-axis parallel to the fibre axis the magnetite showed no evidence of a preferred orientation. Rather, it gave rise to closely spaced, sharp spots lying around Debye arcs. A similar result was obtained by Donnay (1944).

X-ray rotation photographs were also taken of some of the magnetite fibres, intergrown with chrysotile in the asbestos veins of the Shabani specimens. It was found that there is sometimes a strong development of preferred orientation, as evidenced by figures 6.7 and 6.8. The zone axes lying parallel to the fibre axis were determined stereographically (see section 2.3.2.1 of chapter two). The fibre giving rise to the photograph of figure 6.7 was found to have been rotated about an axis $\langle 100 \rangle$, while the photograph of figure 6.8 indicates that an axis $\langle 111 \rangle$ was parallel to the fibre axis. In both instances the repeat period calculated for the particular axis and that indicated by the measured layer line spacing were in good agreement (see captions to figures).

The reasons underlying these particular orientations are not readily apparent, there is no obvious structural match between the sheets of hydroxyls lying parallel to $\langle 100 \rangle$ in the chrysotile fibrils and magnetite in either of the observed orientations. Neither is there any apparent fit of the magnetite structure with pyroaurite in the orientation reported above in chapter five (with an a-axis parallel to the fibre axis). A less surprising orientation would have been with the planes of close-packed oxygens of magnetite (lying parallel to the faces of $\langle 111 \rangle$) arranged parallel to the basal planes of hydroxyls in chrysotile or in pyroaurite; with an axis such as $\langle 110 \rangle$ parallel to the fibre axis.

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CHAPTER SEVEN

The processes involved in serpentinitisation

An attempt will be made in this chapter to relate some of the observations reported in earlier sections to recent ideas on the processes involved in serpentinitisation. There has been considerable discussion of this topic in the literature during the last decade and the review presented here is not exhaustive.

Early discussion hinged upon the apparent conflict between the constant-volume and constant-chemistry theories for serpentinitisation, with few authors adopting the middle ground between these two hypotheses. More recently, isotopic studies have yielded information on the probable temperatures at which pervasive serpentinitisation may have occurred.

7.1 Chemical and volume changes associated with serpentinitisation

Brucite is a widespread accessory mineral in serpentinites, occurring both in primary* lizardite-brucite mesh textures (Wicks, 1969, page 295) and in later cross-cutting veins. The significance of its recognition in serpentinites was discussed by Hostetler et al (1966), who carried out a wide ranging survey of the mineralogy of serpentinitised and partially serpentinitised Alpine-type ultramafics.** They concluded that -

"pervasive serpentinitisation commonly produces significant quantities of brucite, in addition to serpentine group minerals and magnetite"

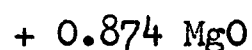
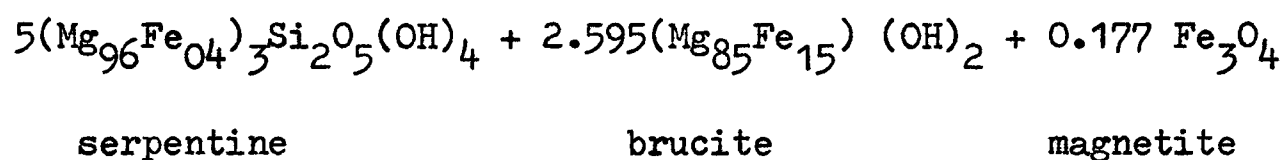
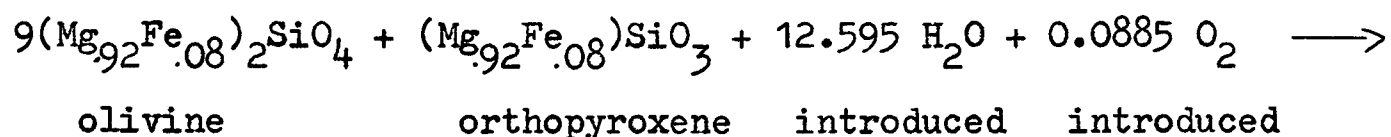
(Hostetler et al, 1966, p. 75).

* The term primary will be used to refer both to the original ultramafic rock (i.e. unserpentinitised) and to the original serpentinite (i.e. not modified by later, near surface, processes).

** See footnote on page 163.

This observation was adduced by Hostetler et al as evidence supporting their contention that serpentinitisation involves considerable volume increase. They did not accept the frequent preservation of olivine grain boundaries and bastites pseudomorphing pyroxene as indisputable evidence favouring an essentially constant volume process of serpentinitisation.

An equation, considered by Hostetler et al to be a typical representation of the serpentinitisation of peridotite was given as follows -



migrated

(Equation (XII), p.90).

This reaction (according to Hostetler et al) involves a volume increase on serpentinitisation of 42.1 per cent, and a migration of Mg⁺⁺ which is slightly more than one per cent of the total rock mass.

Thayer (1966) on the other hand, argued for a process of serpentinitisation which does not involve significant volume changes. He suggested that brucite may be a transitory phase which forms during the early stages of serpentinitisation but disappears as serpentinitisation continues. This view to some extent alleviates the need to demonstrate that (for constant volume serpentinitisation) "truly massive quantities of both silica and magnesia have been removed from the ultramafic mass" (Hostetler et al, 1966, p. 96). It still implies fairly considerable losses of magnesium, however, as can be seen from the equations given by Thayer for the serpentinitisation of olivine and orthopyroxene -

"In any event, serpentinisation is not a constant volume reaction where aqueous solutions flow and yield precipitates spatially distant from the primary minerals dissolved." (p. 268).

It is difficult to see the justification for this statement. The demonstration of the migration of material from the site of serpentinisation would seem to favour, rather than to controvert a constant volume (in the sense of Thayer, 1966) process. If it can be shown that some of the material which is removed from the immediate vicinity of serpentinisation, is reprecipitated within the serpentinised ultramafic mass (presumably as veins) then the volume relationships will be more complicated.

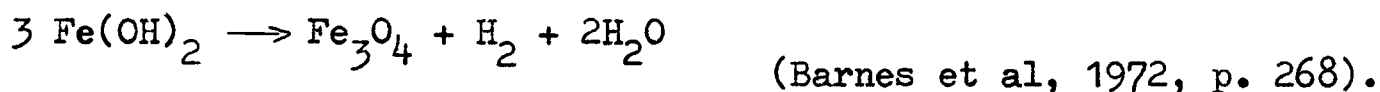
The model for serpentinisation developed by Wicks (1969), in the light of his x-ray studies of the relative orientations of primary olivine and pyroxene and the serpentine minerals, on a "crystal for crystal basis" implies this type of situation. That is to say, a mechanism involving strictly limited increase in the volumes occupied by individual crystals, but requiring "the liberation of large numbers of Mg and Si cations." These cations may on the one hand be retained within the rock body as vein-forming material, implying a considerable overall increase in the total rock volume; on the other hand they may migrate beyond the boundaries of the ultramafic mass, which would necessitate little overall change in rock volume. Presumably some situation intermediate between these two extremes is quite possible.

Barnes et al (1972) pointed out that since $\text{Fe}(\text{OH})_2$ is much less soluble than $\text{Mg}(\text{OH})_2$ the brucite precipitated from solutions which have migrated will be $\text{Fe}(\text{OH})_2$ poor, while that formed near the site of dissolving olivine or orthopyroxene will tend to be more iron-rich.

On this basis, brucite occurring in lizardite-brucite mesh textures and in lizardite-brucite bastites formed from the serpentinisation of olivine and pyroxene respectively, would be expected to be more iron-rich than brucite occurring in cross-cutting veins. Some data on brucite obtained in the present study support this conclusion.

The ferruginosities of brucite samples from veins and host rock of a series of drill core samples from the Jeffrey mine, Quebec were determined, using the x-ray diffraction method described in chapter four. The values obtained are given in Table 7.1. The total number of co-existing vein/host pairs available was small and a fairly wide range of compositions was found within both groups, so that overlap occurs between the ferruginosity values for vein and host-rock brucite. In all cases, however, the host rock brucite showed a higher $\text{Fe}(\text{OH})_2$ content than brucite taken from veins cutting that specimen. The variability in the composition of brucite between samples, which was also noted by Wicks (1969), presumably implies that chemical equilibrium during serpentinitisation was realised over strictly limited volumes.

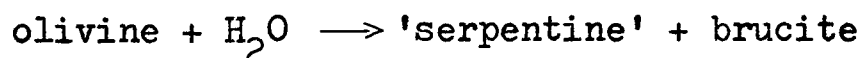
The interpretation of data such as those just described may be complication by the secondary oxidation of Fe-brucite. This may proceed according to a reaction such as -



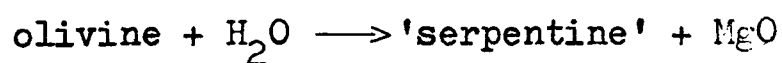
to produce an Fe-poor brucite plus magnetite assemblage from a more iron-rich brucite; see also chapter five for further discussion of the secondary alteration of brucite.

7.2 The temperature and kinetics of reactions involved in serpentinitisation

Hostetler et al (1966) stated that in the light of their recognition of brucite as a widespread product of serpentinitisation, the petrological implications of the reaction -



are enhanced. This reaction implies significantly lower maximum temperatures of serpentinitisation than those suggested by acceptance of a reaction of the type -



(see for example O'Hara, 1967).

TABLE 7.1

$\text{Fe}(\text{OH})_2$ contents of brucite samples from the Jeffrey mine,
estimated by an x-ray diffraction technique

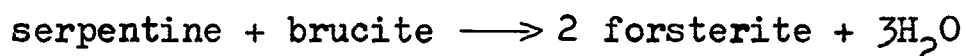
Sample	Brucite from Host rock		Brucite from Veins	
	d_{0001} (Å)	% $\text{Fe}(\text{OH})_2$	d_{0001} (Å)	% $\text{Fe}(\text{OH})_2$
AG67-697	nd		4.763	4.0
-725	4.742	16.0	4.760	5.5
-761	4.765	3.0	4.768	1.0
-857	nd		nd	
-869	nd		nd	
-939	nd		4.758	7.0
-951	4.765	3.0	4.768	1.0
-992	ns		4.764	3.5
-1013	4.766	2.0	4.770	0
-1023	4.758	7.0	4.763	4.0
-1044	4.762	4.5	ns	
-1056	nd		ns	
-1130	ns		4.766	2.0
-1138	4.760	5.5	ns	
-1148	ns		4.761	5.0
-1176	4.763	4.0	4.768	1.0
-1185	4.768	1.0	ns	
-1316	4.765	3.0	ns	

nd - brucite either absent or present in insufficient amount to
permit accurate measurement of peak position

ns - no sample available.

It was suggested by Page (1967), on the basis of thermodynamic calculations, that the stability range of iron-bearing brucite, was likely to be confined to significantly lower temperatures than that of brucite with the composition of the magnesium end-member. While it is not justifiable to attach too much significance to the exact temperature calculated by Page - in view of his assumption of ideal mixing between the two end-member compositions, $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$ - it nevertheless seems reasonable to accept the general implications of his results.

The results published by Scarfe and ^{Wyllie}Wiley (1967) lend support to Page's conclusions. Scarfe and Wiley investigated experimentally the reaction -



as part of an investigation into the tectonic behaviour of serpentinites.

In some runs Scarfe and ^{Wyllie}Wiley investigated the effects of $\text{FeO} + \text{Fe}_2\text{O}_3$ (buffered) in the system and found that this lowered the temperature of dehydration by approximately 100°C , relative to the iron-free system.

Aumento (1970) studied the serpentine mineralogy of samples from ultramafic intrusions in Canada and from the mid-Atlantic ridge. He reported a variation in the cell parameters of lizardite from different serpentinites and attributed this to varying degrees of substitution for Mg and Si, arising from varying temperatures of serpentinisation.

Aumento also estimated the amount of brucite occurring in each of his samples and on the basis of the work of Hostetler et al (1966) estimated temperatures of serpentinisation for several intrusions. He concluded from the evidence of these two lines of investigation that the temperature of serpentinisation of the mid-Atlantic ridge serpentinites was significantly lower than those of the Muskox, Jeffrey mine and Mount Albert intrusions. Aumento suggested temperatures in the range $< 400^\circ\text{C}$ to 485°C .

More recently Wenner and Taylor (1971), on the basis of oxygen isotope studies of coexisting magnetite and serpentine, established a serpentine-magnetite geothermometer which suggested relatively low equilibrium temperatures of serpentinitisation, as follows -

continental lizardite-chrysotile	:	85 to 115°C
oceanic lizardite-chrysotile	:	130°C, 185°C
continental antigorite	:	235°C
oceanic antigorite	:	220 to 460°C

Wenner and Taylor admitted that these temperatures might not be altogether reliable but considered that -

"given our present understanding of the oxygen isotope chemistry of the common rock-forming minerals, it is absolutely inconceivable that serpentine-magnetite Δ - values of 12.9 to 15.1 [the range of values found for 'normal' continental lizardite-chrysotile type serpentinites] could represent equilibrium temperatures any higher than about 150 to 175°C." (p. 183).

One group of serpentinites examined by Wenner and Taylor (termed by them 'anomalous' lizardite-chrysotile type') contained abundant magnetite with variable ($> 5\%$) amounts Cr_2O_3 in solid solution. The isotope data for this group of samples are noticeably irregular, in contrast to the uniform character of the data obtained from 'normal' lizardite-chrysotile serpentinites. The anomalous samples exhibit relatively low Δ - values, which indicate significantly higher equilibrium temperatures (200-300°C) than those found for the 'normal' group ($\sim 100^\circ\text{C}$).

Wenner and Taylor considered that this chromian magnetite had been formed "during a deuteritic or higher temperature hydrothermal event, perhaps accompanying the intrusion of nearby granite bodies" (Wenner and Taylor, 1971, p. 171).

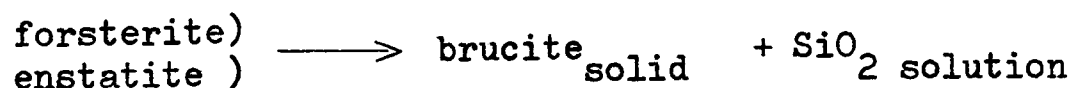
The association of relatively chrome-rich magnetite with secondary replacement textures in serpentinites from Shabani, reported in chapter six may be correlated with Wenner and Taylor's observations. It was suggested in chapter six that these secondary textures might have been developed during some metamorphic event subsequent to serpentinitisation, perhaps associated with the emplacement of granites.

Wenner and Taylor's data do not support the hypothesis of present day serpentinitisation, at temperatures characteristic of weathering processes. This was proposed by Barnes et al (1967), Barnes and O'Neil (1969) and summarised by O'Neil and Barnes (1970) in the following statement -

"The isotope data on carbonates associated with fresh serpentinites and chemically unusual ground waters are part of an increasing body of knowledge supporting present-day serpentinitisation of fresh ultramafic rocks by their interaction with ground waters at near-surface temperatures." *

(O'Neil and Barnes, 1970, p. 696).

The kinetics of the hydration of enstatite and of forsterite were investigated by Martin and Fyfe (1970). In their experiments they found that the percentage conversion to the hydrate increased as the ratio of the amount of solid to the amount of water (S/H_2O) decreased. They suggested that this relationship might arise because brucite formed by the incongruent solution of forsterite and enstatite, "on the surface of the reactant may be the site of subsequent serpentine nucleation" (p.189).



Because of its low solubility the amount of brucite so formed will increase as the relative amount of water is increased.

* This view represents a return to the "weathering theory of serpentinitisation", which was widely held in the late nineteenth century (see Benson, 1918).

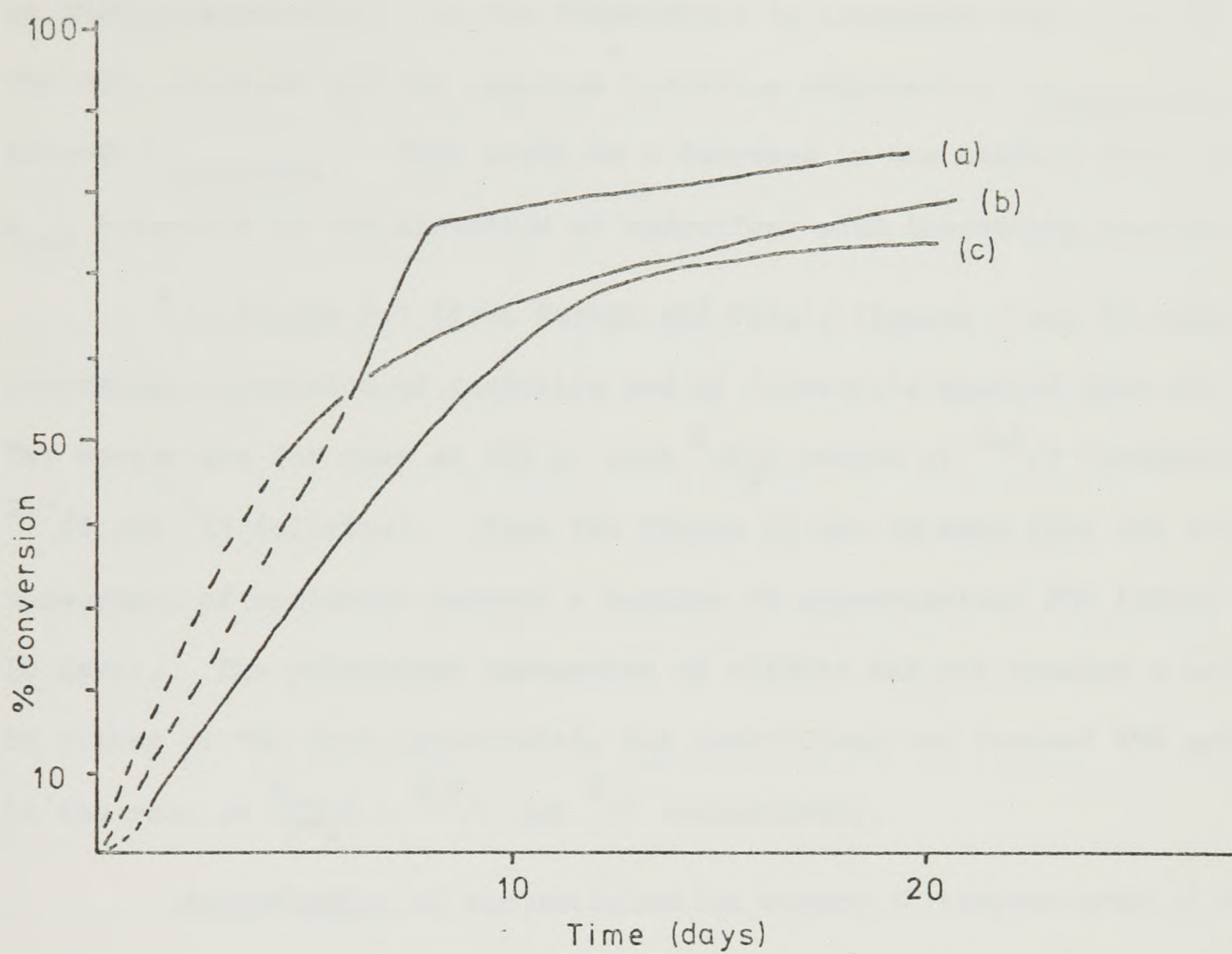


Figure 7.1. Percentage conversion of forsterite and enstatite vs. time in hydration experiments.

(a) Forsterite: 245°C , $\text{S}/\text{H}_2\text{O} = 2.3/1$

(b) Forsterite: 245°C , $\text{S}/\text{H}_2\text{O} = 4/1$

(c) Enstatite : 245°C , $\text{S}/\text{H}_2\text{O} = 2.5/1$

(After Martin and Fyfe 1970, figures 3 and 4).

Martin and Fyfe interpreted their data as indicating that the rate of hydration is at first "interface controlled" (i.e. dependent upon nucleation and growth at certain active sites) but that as the percentage of product increases the reaction becomes at least partly diffusion controlled. They considered that the concept of 'retrograde kinetics' had some application to their experiments. As the temperature is increased above a certain value the rate constant for the reaction involving dehydration ($k_{\text{dehydration}}$) tends towards $k_{\text{hydration}}$. This leads to a decrease in the overall rate of reaction, k_{eff} (measured in the direction of hydration) with increasing temperature.

In figure 7.1 (from Martin and Fyfe's figures 3 and 4) graphs of percentage conversion of enstatite and of forsterite against time are plotted. The curves are for runs at 245°C , with $\text{S}/\text{H}_2\text{O}$ ratios of $2.5/1$ (enstatite) and $2.3/1$ and $4/1$ (olivine). From the figure it can be seen that the percentage conversion of enstatite reached a maximum of approximately 70% (after about 20 days). The percentage conversion of olivine had not reached a maximum in either of the runs illustrated, but nonetheless had reached 85% and 75% in the runs at $\text{S}/\text{H}_2\text{O} = 2.3/1$ and $4/1$ respectively.

Accordingly, if serpentinisation occurs at temperatures of this order as indicated by the work of Wenner and Taylor (1971), then it is likely that under conditions of partial serpentinisation the proportion of olivine converted will be greater than the proportion of pyroxene. This accords well with the frequent observation of relict pyroxene in ultramafic rocks in which almost all of the olivine has been converted to mesh texture serpentine.

Perhaps the most significant points, geologically, to emerge from Martin and Fyfe's experiments are that the hydration reactions involved in serpentinisation are geologically rapid, and that the rate controlling factor in natural systems is almost certainly the rate of diffusion of water to the site of reaction.

If the hydration of an ultramafic body occurs as it rises from depth (see for instance Engin and Hirst (1970)), then there seems to be no reason why primary serpentinitisation should not occur over a wide range of (decreasing) temperatures, the rate and degree of serpentinitisation depending primarily upon the availability and ease of access of water to the ultramafic body.

Wicks (1969) considered that the chemical homogeneity of mesh texture lizardite increased as serpentinitisation progressed, and that this trend could be correlated with variations in the textural development of magnetite (see chapter six). This implies that fairly extensive chemical reorganisation of early formed serpentine textural units continues into the later stages of serpentinitisation, and that the processes involved occur over a range of pressure and temperature. The abundance of magnetite in late, cross-cutting veins in serpentinites also suggests that magnetite remains mobile into the latest stages of serpentinitisation.

In this case emphasis should be laid upon the statement made by Wenner and Taylor to the effect that the equilibrium temperatures indicated by their oxygen isotope studies may provide an estimate of the lower limits to the temperatures of serpentinitisation of the samples investigated, rather than an estimate of the temperature at which pervasive serpentinitisation was initiated.

As was pointed out by Wenner and Taylor, the resolution of this problem would require the characterisation and separation of the successive generations of magnetite. The first of these requirements has already been discussed (chapter 6), the second would present practical difficulties in the separation of sufficient material for isotopic analysis.

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APPENDIX A

Computer Programs

The calculations which formed the basis of the intensity profiles presented in chapters two and three, were performed on a CDC 7600 computer at the University of London Computer Centre, via a link from the Oxford University Computer Centre. The programs were written in Fortran, and were developed in the first instance, using the ICL 1906A computer at Oxford.

The purpose of this appendix is to indicate the way in which the original intensity expressions, given in chapters two and three, were rearranged for computation, and to describe the general structure of the programs. Detailed specification of the data required by each program is given at the end of the listings. Comment cards have been inserted into the text of the programs, with the aim of indicating the operation of the programs and the significance of some of the variables used.

The two programs ORTHO and PARA, which were used to calculate the profiles of diffuse reflections from ortho- and clino-chrysotile and para-chrysotile respectively will be described with reference to the accompanying flow diagram. A program WATES was written to investigate the statistical weights arising from a wide range of fibril size distributions, according to the weighting scheme discussed in section 2.3.1. of chapter two. This program was later incorporated into the main programs ORTHO and PARA, but a listing of WATES is also given.

The method of computation derives from that adopted by Whittaker (1956) and is essentially the same in both ORTHO and PARA. The program ORTHO will be described first.

Subroutine INPUT - Causes the data to be read as follows -

a set of fractional co-ordinates x_j , y_j and z_j for each of the j atoms in the chrysotile layer.

the cell parameters of an individual layer, a , b and c .

the range of layers, m to be considered, m_1 and m_2 .

the range ($k_{\min}$ to $k_{\max}$) and interval (k_{step}) of the variable k to be considered.

k and l , the indices of the reflection Ok_l ; multiplicity and scattering factor values for the j atoms, u_j and f_j .

Subroutine TABLE A -

the value of $\frac{b_{m,j}}{b}$ is calculated for each atom, j in each layer, m .

$$b_{m,j} = \frac{2\pi}{P_m} (ma + x_j)$$

$$\therefore \frac{b_{m,j}}{b} = \frac{m + x_j/a}{m}$$

Subroutine TABLE B -

calculates values of $P_m \frac{b_{m,j}}{b} k$ for each atom, j in each layer, m at each value of k .

$$P_m = \frac{2\pi ma}{b}$$

$$\approx 5m$$

Subroutine TABLE C -

Calculates values of $J_{Kp_m} \left(P_m \frac{b_{m,j}}{b} k \right)$.

Various library programs* were incorporated to calculate values of the Bessel functions of order Kp_m and argument $\left(P_m \frac{b_{m,j}}{b} k \right)$, for each of the atoms, j in each layer, m at each value of k .

* Available at O.U.C.C. in OXLIB 1900 BESSJØ, BESSJI and BESSJN were used to calculate functions of orders zero, one and n (n is an integer of > 1) respectively.

Subroutine TABLE D -

The expression -

$$u_j f_j \exp \left[2\pi i l \frac{z_j}{c} \right] \cos 2\pi \frac{K y_j}{b}$$

abstracted from equation 2.1 can be written as -

$$u_j f_j \cos 2\pi \frac{K y_j}{b} \left(\cos 2\pi \frac{l z_j}{c} + \sin 2\pi \frac{l z_j}{c} \right)$$

In this subroutine two values are calculated for each atom, j in each layer, m at each value of k, viz -

$$1) u_j f_j \cos 2\pi \frac{K y_j}{b} \sin 2\pi \frac{l z_j}{c}$$

$$2) u_j f_j \cos 2\pi \frac{K y_j}{b} \sin 2\pi \frac{l z_j}{c}$$

Each of these values is multiplied by the appropriate value of J_{Kp_m} $(Pm \frac{b m, j}{b} k)$ from TABLE C.

Subroutine TABLE F -

The two sets of values produced in TABLE D are each summed over the j atoms at constant k, for each layer, m. The resulting sums are squared and corresponding squared values from each set are added together, to produce a single set of intensity contributions from each layer, m to the reflection Okl at each value of k considered.

Subroutine WATES -

This subroutine causes sets of weighting parameters to be read as follows -

m_0 the value of m for the neutral (strain-free) layer.

mw_1, mw_2 the range of layers to be included in the summation.

t a constant.

For each set of parameters the appropriate statistical weights are applied to the contributions from each layer, m at each value of k and the resulting values are summed over the required number of layers. The weighted intensity profiles are output to a lineprinter, as a series of tables.

Subroutine NEWD -

If required, a new set of values $k_{\min}$, $k_{\max}$ and k_{step} can be read. This allowed the profile of a reflection to be calculated section by section, to diminish the risk of the program exceeding its allotted time and thus losing all results from that run.

The calculations of the profiles of reflections from para-chrysotile are based upon equation 3.1. The program PARA differs only in detail from ORTHO and it will be described with reference to the same flow diagram.

Subroutine INPUT -

This fulfills the same function as in ORTHO, except that the variables $k_{\min}$, $k_{\max}$ and k_{step} are replaced by $l_{\min}$, $l_{\max}$ and l_{step} respectively, since we are concerned with the profile of a reflection OkL at constant k and with respect to a continuously variable l parameter.

Subroutine TABLE A -

Calculates the values of $\frac{c_{m,j}}{c}$ for each atom, j in each layer, m

$$\frac{c_{m,j}}{c} = \frac{m + \frac{x_j}{a}}{m}$$

Subroutine TABLE B -

Calculates values of $P_m \frac{c_{m,j}}{c} l$ for each atom, j in each layer, m at each value of l

$$P_m = \frac{2\pi m a}{c}$$

$$\approx 8.5 m$$

Subroutine TABLE C -

Calculates values of $J_{Lp_m}^{cm,j}(\rho_m \frac{j}{c} l)$ for each atom, j in each layer, m at each value of l . If both m and L are odd then the order of the Bessel function, Lp_m will be half integral and the relationship that

$$J_{n+\frac{1}{2}}(z) = j_n(z) / \sqrt{\pi/2} / z$$

must be used to calculate the required values. The spherical Bessel functions, j_n were calculated using the library program SPHEJN, incorporated as a subroutine into PARA. When either m or L is even the Bessel functions are calculated using BESSJØ, BESSJI and BESSJN as in ORTHO.

Subroutine TABLE D -

The values of A and B in equations 3.2 and 3.3 (appropriate to the two-fold and four-fold atoms respectively) are evaluated for each atom, j in each layer, m at each value of l .

Subroutine TABLE F -

The sets of values of A and B derived in TABLE D are each summed over the j atoms, at constant values of m and l . The sums obtained are squared, and corresponding results from each set added together, to give a set of intensity contributions from each layer, m to the reflection OkL at each value of l considered.

Subroutine WATES -

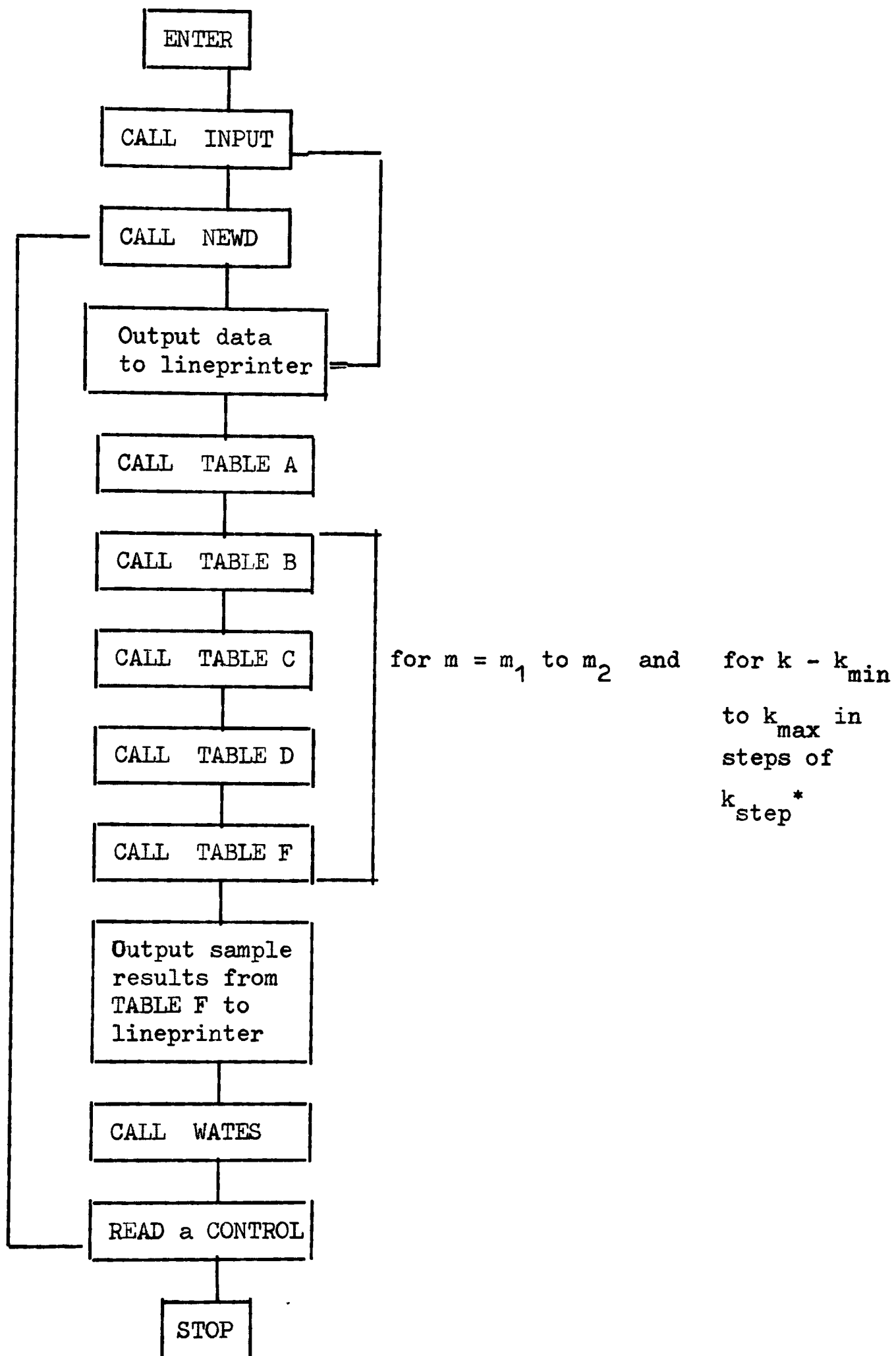
The variables m_0 , mw_1 and mw_2 and t are read as in ORTHO, together with two further variables, il and ol which give the range of layers to be included in a summation in which each layer is given unit weight. The appropriate statistical weights are applied and summations over the specified ranges of layers are carried out. The results are then output to a lineprinter in the form of two sets of tables. One set gives intensity profiles from fibre bundles, the other set profiles appropriate to individual fibrils.

Subroutine NEWD -

This subroutine was included for the same reason as in ORTHO

The profile of the 031 reflection of ortho- or clino-chrysotile, based upon a special type of helical lattice was discussed briefly in section 2.3.1. A listing of the program, ORTHOH written to perform the necessary calculations is given, but since this program differs only slightly in its operation from ORTHO it is not described.

Flow diagram for programs ORTHO and PARA



* k should be replaced by 1 in the case of PARA

REFERENCES

WHITTAKER, E.J.W.

1956. The structure of chrysotile and crocokolite. Ph.D thesis, University, London.

#LISTING OF :GEOL.ANDY2(1/) PRODUCED ON 17JAN74 AT 22.22.14
#OUTPUT BY LISTFILE IN ':GEOL.MOPCMS' ON 17JAN74 AT 22.53.55

DOCUMENT ANDY2

```

C**** PROGRAM PARA ****
PROGRAM PARA(INPUT,OUTPUT,TAPE 5=INPUT,TAPE 6=OUTPUT)
INTEGER TM
REAL COORDS(9,3),LMIN,LMAX,LSTEP,L,LPR,UJ(9),FJ(9)
DIMENSION TABA(9,75),TABD(9),TARE(9),TABF(75,100)
C COMMON BLOCK DATA PASSES DATA
COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTFST,
1LSTEP
C COMMON BLOCK VALS PASSES RESULTS
COMMON/VALS/TABA,TABB,TABC,TABD,TABE
C COMMON BLOCK FRES PASSES RESULTS FROM TABLEF
COMMON/FRES/TABF
LEVEL 2,TABF
CALL INPUT
TM=MTST
GO TO 101
100 CALL NEWD
WRITE(6,6008)
6008 FORMAT(2H1 //12H NEWD CALLED//)
101 CONTINUE
C OUTPUT DATA
WRITE(6,6006)A,B,C,M1,M2,LMIN,LMAX,LSTEP,KR,LR
6006 FORMAT(11H DATA GIVEN//3H A=,
1F10.4,5X,4H B= ,F10.4,5X,4H C= ,F10.4//
25H M1= ,14,5X,5H M2= ,14,5X
3//7H LMIN= ,F10.4,5X,
46H LMAX=,F10.4,7H LSTEP=,F10.4//5H KR= ,14,5X,5H LR= ,14)
WRITE (6,6004)
6004 FORMAT(///23H VALUES OF COORDINATES /15X,2H X,9X,2H Y,8X,2H Z/)
DO 57 J=1,9
WRITE(6,6005)J,(COORDS(J,I),I=1,3)
57 CONTINUE
6005 FORMAT(3H J=,12,5X,3F10.4)
WRITE(6,6003)
6003 FORMAT(///20H VALUES OF UJ AND FJ//
112X,20H UJ FJ /)
WRITE(6,6007)((J,UJ(J),FJ(J)),J=1,9)
6007 FORMAT(4H J= ,12,5X,2F10.4)
C SET VALUE OF L
L=LMIN
CALL TABLEA
C SET UP LOOP FOR STEPS IN L
DO 30 LC=1,100
C SET UP LOOP FOR NUMBER OF LAYERS
DO 20 MC=M1,M2
FMC=FLOAT(MC)
C CALCULATE VALUE OFP(M)
FPM=8.5*FMC
C SET UP LOOP FOR ATOMS J
DO 10 J=1,9
C IFUJ = ZERO SKIP UNNECESSARY CALCULATIONS
IF(UJ(J))14,14,1
1 CONTINUE
C AVOID UNNECESSARY CALCULATIONS FOR ATOMS WITH THE SAME X COORDINATES
GO TO (11,11,11,11,12,11,12,11,12),J
11 CALL TABLEB(J,L,MC,FPM)

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```

      CALL TABLEC(FPM)
12    CALL TABLED(J,MC)
      GO TO 10
14    TABD(J)=0.0
      TABE(J)=0.0
10    CONTINUE
      CALL TABLEF(MC,LC)
20    CONTINUE
C INCREMENT L
      L=L+LSTEP
      IF(L.GT.LMAX) GO TO 13
30    CONTINUE
C SET KOUNT TO LC, THE NUMBER OF STEPS OF L
13    KOUNT=LC
C OUTPUT SAMPLE RESULTS FROM TABLEF
      WRITE(6,6000)
6000  FORMAT(2H1 ,45X,10H TABLES F /)
      M1A2=M1+2
      DO 45 MCC=M1,M1A2
      WRITE(6,6002)MCC
6002  FORMAT(/3H M=,I4)
      LPR=LMIN
      DO 45 LCC=1,KOUNT
      WRITE(6,6001)LPR,TABF(MCC,LCC)
6001  FORMAT(3H L=,F7.4,5X,F10.4)
      LPR=LPR+LSTEP
45    CONTINUE
      CALL WATES(KOUNT)
C MORE IS A PROGRAM CONTROL
      READ(5,5000)MORE
5000  FORMAT(I4)
C IF MORE > ZERO CALL NEWD
      IF(MORE)9,9,100
9      CONTINUE
      STOP
      END
      SUBROUTINE INPUT
C READS IN DATA
      REAL COORDS(9,3),LMIN,LMAX,UJ(9),FJ(9),LSTEP
      COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1 LSTEP
      READ(5,5000)((COORDS(I,J),J=1,3),I=1,9)
5000  FORMAT(3F10.0)
5001  FORMAT(F10.0)
      READ(5,5000)A,B,C
      READ(5,5002)M1,M2
5002  FORMAT(2I4)
      READ(5,5000)LMIN,LMAX,LSTEP
      READ(5,5002)KR,LR
      READ(5,5001)(UJ(I),I=1,9)
      READ(5,5001)(FJ(I),I=1,9)
      WRITE(6,6000)
6000  FORMAT(/,20H1 INPUT SUCCESSFUL )
      RETURN
      END
      SUBROUTINE TABLEA
C CALCULATE VALUES OF C(M,J)/C
      REAL COORDS(9,3),LMIN,LMAX,UJ(9),FJ(9),LSTEP
      DIMENSION TABA(9,75),TABD(9),TABE(9)
      COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1 LSTEP
      COMMON/VALS/TABA,TABB,TABC,TABD,TABE
      DO 14 J=1,9
C IF UJ = ZERO AVOID UNNECESSARY CALCULATIONS
      IF(UJ(J))8,14,8
8      CONTINUE

```

```

C AVOID CALCULATIONS FOR THE J TH ATOM WITH THE SAME X COORDINATES
C AS THE J-1 TH ATOM
      GO TO (11,11,11,11,12,11,12,11,12) , J
11    CONTINUE
      DO 10 I=M1,M2
      FI=FLOAT(I)
C ASSIGN VALUES FOR THE J TH ATOM IN THE I TH LAYER
      TABA(J,I)=(FI+COORDS(J,1))/FI
10    CONTINUE
      GO TO 14
12    CONTINUE
      DO 13 I=M1,M2
      TABA(J,I)=TABA(J-1,I)
13    CONTINUE
14    CONTINUE
      RETURN
      END
      SUBROUTINE TABLEB(J,L,MC,FPM)
C CALCULATE P(M)*(C(M,J)/C)*L
      REAL LMIN,LMAX,LSTEP,L,COORDS(9,3),UJ(9),FJ(9)
      DIMENSION TABA(9,75),TABD(9),TABE(9)
      COMMON/VALS/TABA,TABB,TABC,TABD,TABE
      COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1LSTEP
      TABB=FPM*TABA(J,MC)*L
      RETURN
      END
      SUBROUTINE TABLEC(FPM)
      REAL L,LMIN,LMAX,LSTEP,COORDS(9,3),UJ(9),FJ(9),
1BFLIB(2000),BFLIB2(2000),SBF(2000),SBF2(2000)
      DIMENSION TABA(9,75),TABD(9),TABE(9)
      COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1LSTEP
      COMMON/VALS/TABA,TABB,TABC,TABD,TABE
      X=0.0
      FLR=FLOAT(LR)
      FIR=FPM*FLR
C IR IS THE ORDER OF THE BESSEL FUNCTION REQUIRED
      IR=IFIX(FIR)
C TEST WHETHER BESSEL FUNCTION IS OF INTEGRAL ORDER
      FIR2=FLOAT(IR)
      D=FIR-FIR2
      IF(D.GT.0.4) GO TO 102
C CALL BESSJO IF IR = ZERO
      IF(IR.EQ.0) GO TO 17
C PROCEDURE FOR INTEGRAL ORDERS
C BFLIB(IR+1) CONTAINS THE VALUE OF BESSEL FUNCTION OF ORDER IR
      CALL BESSJN(TABB,X,BFLIB,BFLIB2,IR)
      TABC=BFLIB(IR+1)
      GO TO 20
17    CONTINUE
      CALL BESSJO(TABB,X,BF1,BF2)
      TABC=BF1
20    CONTINUE
      GO TO 103
102   CONTINUE
C PROCEDURE FOR HALF-INTEGER ORDERS, IF M= ODD & L=ODD
C SBF(X+1) CONTAINS THE VALUE OF THE BESSEL FUNCTION OF ORDER X
      CALL SPHEJN(TABB,SBF,SBF2,IR)
      TABC=SBF(IR+1)/(SQRT(1.5708/TABB))
103   CONTINUE
      RETURN
      END
      SUBROUTINE TABLED(J,MC)
      REAL L,LMIN,LMAX,LSTEP,COORDS(9,3),UJ(9),FJ(9),
1TD1(9),TD2(9),TD3(9),TD4(9),TD5(9),TD6(9)

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        DIMENSION TABA(9,75),TABD(9),TABF(9)
        COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1 LSTEP
        COMMON/VALS/TABA,TABB,TABC,TABD,TABE
C TD1 ETC ARE CONSTANT FOR A GIVEN VALUE OF J AT ANY VALUE OF M; THEY
C ARE THEREFORE CALCULATED ONLY ONCE FOR EACH VALUE OF J
        IF(MC.GT,M1) GO TO 100
        FK=FLOAT(KR)
        FL=FLOAT(LR)
        TD1(J)=UJ(J)*FJ(J)
        TD2(J)=COS(6.2832*FK*COORDS(J,2))
        TD3(J)=COS(6.2832*FL*COORDS(J,3))
        TD4(J)=SIN(6.2832*FL*COORDS(J,3))
        TD5(J)=TD1(J)*TD2(J)*TD3(J)
        TD6(J)=TD1(J)*TD2(J)*TD4(J)
100 CONTINUE
        GO TO (10,11,11,11,10,10,11,10,11),J
10 TABD(J)=TABC*TD1(J)*TD3(J)
    TABE(J)=TABC*TD1(J)*TD4(J)
    GO TO 33
11 TABD(J)=TABC*TD5(J)
    TABE(J)=TABC*TD6(J)
33 CONTINUE
    RETURN
    END
    SUBROUTINE TABLEF(MC,LC)
C SUM CONTRIBUTIONS FROM ALL J ATOMS IN EACH LAYER
    REAL LMIN,LMAX,LSTEP,COORDS(9,3),UJ(9),FJ(9)
    DIMENSION TABA(9,75),TABD(9),TABE(9),TABF(75,100)
    COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,MTEST,
1 LSTEP
    COMMON/VALS/TABA,TABB,TABC,TABD,TABE
    COMMON/FRES/TABF
    LEVEL 2,TABF
C SET TF1,TF2
    TF1=0.0
    TF2=0.0
C SUM OVER J ATOMS
    DO 10 J=1,9
        TF1=TF1+TABD(J)
        TF2=TF2+TABE(J)
10 CONTINUE
C SQUARE THE SUMS
    TF1=TF1*TF1
    TF2=TF2*TF2
C ADD THE SQUARES
    TABF(MC,LC)=TF1+TF2
    RETURN
    END
    SUBROUTINE NEWD
C COLLECT NEW RANGE OF L
    REAL LMIN,LMAX,LSTEP,UJ(9),FJ(9),COORDS(9,3)
    COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,UJ,FJ,
1 MTEST,LSTEP
    READ(5,5002)LMIN,LMAX,LSTEP
5002 FORMAT(3F10.0)
    RETURN
    END
    SUBROUTINE WATES(KOUNT)
C APPLY WEIGHTS TO RESULTS FROM TABLEF
    INTEGER OL
    REAL LMIN,LMAX,LSTEP,UJ(9),FJ(9),COORDS(9,3)
    DIMENSION TABF(75,100),V(75),WF(75),PMSQ(75),RES(100)
1,RES2(100)
    COMMON/FRES/TABF
    COMMON/DATA/COORDS,A,B,C,M1,M2,LMIN,LMAX,KR,LR,

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10J,FJ,MTEST,LSTEP
LEVEL 2,TABF
C HEADING
WRITE(6,6000)
6000 FORMAT(//20H RESULTS FROM WATES //)
5000 FORMAT(3I4)
5001 FORMAT(F10.0)
DO 10 I=M1,M2
FI=FLOAT(I)
PMSQ(I)=(8.5*FI)**2
10 CONTINUE
20 READ(5,5000)M0,MW1,MW2
C IF M0<= ZERO RETURN TO MAIN PROGRAM
IF(M0)14,14,11
11 READ(5,5001)T
READ(5,5002)IL,OL
5002 FORMAT(2I4)
C CALCULATE THE WEIGHTS
FM0=FLOAT(M0)
R=1.0/FM0
DO 12 I=MW1,MW2
FI=FLOAT(I)
X=((1.0/FI)-R)**2)*T*FI
IF (X.EQ.0.0) GO TO 13
Y(I)=EXP(-X)
GO TO 12
13 Y(I)=1.0
12 CONTINUE
C SET WEIGHT OF NEUTRAL LAYER TO ONE
WF(M0)=1.0
I=M0+1
MW2S1= MW2-1
DO 70 J=M0,MW2S1
WF(I)=WF(I-1)*Y(I)
I=I+1
70 CONTINUE
I=M0-1
M0S1=M0-1
DO 71 J=MW1,M0S1
WF(I)=WF(I+1)*Y(I)
I=I-1
C WEIGHT FOR THE I TH LAYER IS IN WF(I)
71 CONTINUE
DO 15 L=1,KOUNT
A2=0.0
A1=0.0
C APPLY WEIGHTS AND SUM CONTRIBUTIONS FROM REQUIRED LAYERS; RESULTS IN
DO 16 MC=MW1,MW2
B1=TABF(MC,L)*PMSQ(MC)*WF(MC)
A1=A1+B1
16 CONTINUE
C PUT RESULTS INTO RES(L)
RES(L)=A1
C APPLY UNIT WEIGHTING SCHEME
C PUT RESULTS INTO RES2(L)
DO 17 ML=IL,OL
B2=TABF(ML,L)*PMSQ(ML)
A2=A2+B2
17 CONTINUE
RES2(L)=A2
15 CONTINUE
C OUTPUT RESULTS
WRITE(6,6001)KR,LR,MW1,MW2,M0,KP,LR,T,IL,OL
C HEADINGS
6001 FORMAT(//25H PROFILE OF REFLECTION 0,I1,I1/
17H LAYERS,I4,3H TO,I4,11H CONSIDERED/

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216H NEUTRAL LAYER =,I3,20X,
320X,25H PROFILE OF REFLECTION 0,I1,I1/
413H VALUE OF T =,F8.2,16X,
522X,21H UNIT WEIGHTS LAYERS ,I3,3H TO,I3,
611H CONSIDERED/)
    RL=LMIN
    DO 19 L=1,KOUNT
    WRITE(6,6002)RL,RES(L),RL,RES2(L)
6002  FORMAT(2(3H L=,F7.4,5X,F15.4,20X))
    RL=RL+LSTEP
19    CONTINUE
    GO TO 20
14    CONTINUE
    RETURN
    END
    SUBROUTINE SPHEJN(X,U,V,N)
C OXLIB 1900 LIBRARY PROGRAM
    INTEGER A,B,C,D,E,F,G
    DIMENSION U(1000),V(1000)
    K=N+10
3    IF(K.GT.2000) GO TO 5
    FN3=0.0
    FN2=1.0
    J=K+N
    J2=K+N
    DO 1 I=1,J2
    FN1=FLOAT(2*(J-N)+1)*FN2/X-FN3
    IF(ABS(FN1).GT.1.0E20) GO TO 10
    GO TO 11
10    FN1=FN1/1.0E20
    FN2=FN2/1.0E20
    IF((J+1).GT.(2*N+1)) GO TO 11
    A=J+1
    B=2*N+1
    DO 12 L=A,B
    IF(L.LT.(N+1)) GO TO 13
    C=L-N
    U(C)=U(C)/1.0E20
    GO TO 12
13    D=N-L+1
    V(D)=V(D)/1.0E20
12    CONTINUE
11    IF(J.GT.(2*N+1)) GO TO 2
    IF(J.GT.N) GO TO 14
    E=N-J+1
    V(E)=FN1
    GO TO 2
14    F=J-N
    U(F)=FN1
2    FN3=FN2
    FN2=FN1
1    J=J-1
    U0=SIN(X)/X
    U1=SIN(X)/(X*X)-COS(X)/X
    P=U0/U(1)
    G=N+1
    DO 4 I=1,G
4    U(I)=U(I)*P
    DO 6 I=1,N
6    V(I)=V(I)*P
    K=K+10
    P=ABS(U(2)-U1)
    IF(P.GT.0.000000001) GO TO 3
5    RETURN
    END
    SUBROUTINE BESSJO(X,PHI,U0,V0)

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C OXLIB 1900 LIBRARY PROGRAM

```

      IF(X.NE.0,0) GO TO 10
      U0=1.0
      V0=0.0
      RETURN
10  N=1
      IF(PHI.LT.0.0) N=-1
      ARG=ABS(PHI)
      IF(ARG.GE.3.14159265358979) ARG=ARG-3.14159265358979
      IF(X.GE.10.0) GO TO 11
      X1=X/2.0
      ZARG=ARG+ARG
      FAC=1.0
      DO 21 K=1,100
      FAC=FAC*X1/FLOAT(K)
      IF(ABS(FAC).LT.1.0E-10) GO TO 25
21  CONTINUE
      K=100
25  FK=FLOAT(K)
      U0=FAC*FAC*COS(FK*ZARG)
      V0=FAC*FAC*SIN(FK*ZARG)
      J=MOD(K,2)
      IF(J.EQ.0) GO TO 26
      U0=-U0
      V0=-V0
26  M=K
      DO 22 L=2,M
      K=K-1
      FAC=FAC*FLOAT(K+1)/X1
      FAX=FAC*FAC
      J=MOD(K,2)
      IF(J.EQ.0) GO TO 23
      FAX=-FAX
23  FK=FLOAT(K)
      U0=U0+FAX*COS(FK*ZARG)
      V0=V0+FAX*SIN(FK*ZARG)
22  CONTINUE
      U0=U0+1.0
      GO TO 12
11  C=SQRT(2.0/(X*3.14159265358979))
      A=C*COS(ARG/2.0)
      B=-C*SIN(ARG/2.0)
      C=COS(-3.14159265358979/4.0)
      S=SIN(-3.14159265358979/4.0)
      CA=COS(ARG)*X
      SA=SIN(ARG)*X
      CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
      CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S
      SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
      SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
      P=(3.0*3.0)/(2.0*2.0**6.0*X**2.0)
      Q=1.0/(2.0*2.0**6.0*X**2.0)
      P1=P
      Q1=Q
      DO 1 K=2,100
      P=P*(FLOAT(4*K-1)*FLOAT(4*K-1)*FLOAT(4*K-3)*FLOAT(4*K-3))/
1  (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
      Q=Q*(FLOAT(4*K-3)*FLOAT(4*K-3)*FLOAT(4*K-5)*FLOAT(4*K-5))/
1  (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
      IF((P.LT.1.0E-10).AND.(Q.LT.1.0E-10)) GO TO 2
      IF((P.LE.P1).AND.(Q.LE.Q1)) GO TO 8
      P=P1
      Q=Q1
      GO TO 9
8  P1=P
      Q1=Q

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```

1 CONTINUE
  K=100
  GO TO 2
9 K=K-1
2 Q=Q*FLOAT(2*K)*FLOAT(2**3)*X
  J=MOD(K,2)
  IF(J.EQ.0) GO TO 3
  I=-1
  GO TO 4
3 I=1
4 FI=FLOAT(I)
  FK=FLOAT(K)
  PR=FI*P*COS(2.0*FK*ARG)
  PI=-FI*P*SIN(2.0*FK*ARG)
  QR=FI*Q*COS(2.0*FK*ARG-ARG)
  QI=-FI*Q*SIN(2.0*FK*ARG-ARG)
  M=K
  DO 5 L=2,M
    K=K-1
    P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
      1(FLOAT(4*K+3)*FLOAT(4*K+3)*FLOAT(4*K+1)*FLOAT(4*K+1))
    Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
      1(FLOAT(4*K+1)*FLOAT(4*K+1)*FLOAT(4*K-1)*FLOAT(4*K-1))
    J=MOD(K,2)
    IF(J.EQ.0) GO TO 6
    I=-1
    GO TO 7
6 I=1
7 FI=FLOAT(I)
  FK=FLOAT(K)
  PR=PR+FI*P*COS(2.0*FK*ARG)
  PI=PI-FI*P*SIN(2.0*FK*ARG)
  QR=QR+FI*Q*COS(2.0*FK*ARG-ARG)
  QI=QI-FI*Q*SIN(2.0*FK*ARG-ARG)
5 CONTINUE
  PR=PR+1.0
  U0=A*(PR*CR-PI*CI-QR*SR+QI*SI)-B*(PI*CR+PR*CI-QI*SR-QR*SI)
  V0=A*(PI*CR+PR*CI-QI*SR-QR*SI)+B*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(N.EQ.1) GO TO 13
  V0=-V0
13 RETURN
  END
  SUBROUTINE BESSJ1(X,PHI,U1,V1)
C OXLIB 1900 LIBRARY PROGRAM
  IF(X.NE.0.0) GO TO 10
  U1=0.0
  V1=0.0
  RETURN
10 N=1
  IF(PHI.LT.0.0) N=-1
  ARG=ABS(PHI)
  IF(ARG.GE.3.14159265358979) ARG=ARG-3.14159265358979
  IF(X.GE.10.0) GO TO 11
  X1=X/2.0
  ZARG=ARG+ARG
  A=COS(ARG)
  B=SIN(ARG)
  FAC=1.0
  DO 21 K=1,100
    FAC=FAC*X1/FLOAT(K)
    IF(ABS(FAC).LT.1.0E-10) GO TO 25
21 CONTINUE
  K=100
25 FK=FLOAT(K)
  U0=FAC*FAC*FLOAT(K)*COS(FK*ZARG)
  V0=FAC*FAC*FLOAT(K)*SIN(FK*ZARG)

```

```

      J=MOD(K,2)
      IF(J,EQ,0) GO TO 26
      U0=-U0
      V0=-V0
26  M=K
      DO 22 L=2,M
      K=K-1
      FAC=FAC*FLOAT(K+1)/X1
      FAX=FAC*FAC
      J=MOD(K,2)
      IF(J,EQ,0) GO TO 23
      FAX=-FAX
23  FK=FLOAT(K)
      U0=U0+FAX*FLOAT(K)*COS(FK*ZARG)
      V0=V0+FAX*FK*SIN(FK*ZARG)
22  CONTINUE
      U0=U0/X1
      V0=V0/X1
      U1=-(U0*A+V0*B)
      V1=U0*B-V0*A
      GO TO 12
11  C=SQRT(2.0/(X*3.14159265358979))
      A=C*COS(ARG/2.0)
      B=-C*SIN(ARG/2.0)
      C=COS(-3.14159265358979*0.75)
      S=SIN(-3.14159265358979*0.75)
      CA=COS(ARG)*X
      SA=SIN(ARG)*X
      CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
      CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S
      SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
      SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
      P=3.0*5.0/(2.0*2.0**6.0*X**2.0)
      Q=3.0/(2.0*2.0**6.0*X**2.0)
      P1=P
      Q1=Q
      DO 1 K=2,100
      P=P*FLOAT(4-(4*K-1)*(4*K-1))*FLOAT(4-(4*K-3)*(4*K-3))/
1 (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
      Q=Q*FLOAT(4-(4*K-3)*(4*K-3))*FLOAT(4-(4*K-5)*(4*K-5))/
1 (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
      IF((P.LT.1.0E-10).AND.(Q.LT.1.0E-10)) GO TO 2
      IF((P.LE.P1).AND.(Q.LE.Q1)) GO TO 8
      P=P1
      Q=Q1
      GO TO 9
8  P1=P
      Q1=Q
1  CONTINUE
      K=100
      GO TO 2
9  K=K-1
2  Q=Q*FLOAT(2*K)*FLOAT(2**3)*X
      J=MOD(K,2)
      IF(J,EQ,0) GO TO 3
      I=1
      GO TO 4
3  I=1
4  FI=FLOAT(I)
      FK=FLOAT(K)
      PR=FI*P*COS(2.0*FK*ARG)
      PI=-FI*P*SIN(2.0*FK*ARG)
      QR=FI*Q*COS(2.0*FK*ARG-ARG)
      QI=-FI*Q*SIN(2.0*FK*ARG-ARG)
      M=K
      DO 5 L=2,M

```

```

      K=K-1
      P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4-(4*K+3)*(4*K+3))*FLOAT(4-(4*K+1)*(4*K+1)))
      Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4-(4*K+1)*(4*K+1))*FLOAT(4-(4*K-1)*(4*K-1)))
      J=MOD(K,2)
      IF(J.EQ.0) GO TO 6
      I=1
      GO TO 7
6 I=-1
7 FI=FLOAT(I)
  FK=FLOAT(K)
  PR=PR+FI*P*COS(2.0*FK*ARG)
  PI=PI-FI*P*SIN(2.0*FK*ARG)
  QR=QR+FI*Q*COS(2.0*FK*ARG-ARG)
  QI=QI-FI*Q*SIN(2.0*FK*ARG-ARG)
5 CONTINUE
  PR=PR+1.0
  U1=A*(PR*CR-PI*CI-QR*SR+QI*SI)-R*(PI*CR+PR*CI-QI*SR-QR*SI)
  V1=A*(PI*CR+PR*CI-QI*SR-QR*SI)+R*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(ABS(PHI).LT.3.14159265358979) GO TO 13
  U1=-U1
  V1=-V1
13 IF(N.EQ.-1) V1=-V1
  RETURN
  END
  SUBROUTINE BESSJN(X,PHI,U,V,N)
C OXLIB 1900 LIBRARY PROGRAM
  DIMENSION U(2),V(2)
  IF(X.NE.0.0) GO TO 30
  U(1)=1.0
  V(1)=0.0
  DO 31 I=1,N
  U(I+1)=0.0
  V(I+1)=0.0
31 CONTINUE
  RETURN
30 NN=1
  IF(PHI.LT.0.0) NN=-1
  ARG=ABS(PHI)
  IF(ARG.GE.3.14159265358979) ARG=ARG-3.14159265358979
  FN=FLOAT(N)
  IF(X.LE.FN) GO TO 1
  CALL BESSJ0(X,ARG,U(1),V(1))
  IF(N.LT.1) GO TO 20
  CALL BESSJ1(X,ARG,U(2),V(2))
  IF(N.LT.2) GO TO 20
  DO 10 I=2,N
  U(I+1)=(2.0*FLOAT(I-1)*U(I)*COS (ARG)+2.0*FLOAT(I-1)*V(I)*
1 SIN (ARG))/X-U(I-1)
  V(I+1)=(2.0*FLOAT(I-1)*V(I)*COS (ARG)-2.0*FLOAT(I-1)*U(I)*
1 SIN (ARG))/X-V(I-1)
10 CONTINUE
  GO TO 20
  1 N1=N+1
  IX=IFIX(X)
  K=IX+20
  IF(K.LT.N) K=N
  2 SCAR=1000000.0
  SCAI=1000000.0
  STRR=0.0000001
  STRI=0.0000001
  WAR=STRR
  WAI=STRI
  WBR=0.0
  WBI=0.0

```

```

J=K+1
DO 5 I=1,K
J=J-1
WCR=(2.0*FLOAT(J)*WAR*COS (ARG)+2.0*FLOAT(J)*WAI*SIN (ARG))/X-WRR
WCI=(2.0*FLOAT(J)*WAI*COS (ARG)-2.0*FLOAT(J)*WAR*SIN (ARG))/X-WRI
WBR=WAR
WBI=WAI
WAR=WCR
WAI=WCI
IF((J-1).GT.N) GO TO 4
U(J)=WCR
V(J)=WCI
4 IF((ABS(WCR).LE.SCAR).AND.(ABS(WCI).LE.SCAI)) GO TO 3
WAR=WAR/SCAR
WBR=WBR/SCAR
STRP=STRR/SCAR
IF(J.GT.N1) GO TO 8
DO 6 L=J,N1
U(L)=U(L)/SCAR
6 CONTINUE
8 CONTINUE
WAI=WAI/SCAI
WBI=WBI/SCAI
STRI=STRI/SCAI
IF(J.GT.N1) GO TO 3
DO 9 L=J,N1
V(L)=V(L)/SCAI
9 CONTINUE
3 CONTINUE
CALL BESSJO(X,ARG,UL,VL)
ULAM=(UL*U(1)+VL*V(1))/(U(1)**2+V(1)**2)
VLAM=(VL*U(1)-UL*V(1))/(U(1)**2+V(1)**2)
IF((ABS (STRR*ULAM).LE.0.00000000001).AND.(ABS (STRI*VLAM).LE.
10.00000000001)) GO TO 5
K=K+10
GO TO 2
5 DO 7 L=1,N1
UU=U(L)
VV=V(L)
U(L)=UU*ULAM-VV*VLAM
V(L)=VV*ULAM+UU*VLAM
7 CONTINUE
20 IF(ABS(PHI).LT.3.14159265358979) GO TO 21
DO 22 I=1,N
K=MOD(I,2)
IF(K.EQ.0) GO TO 22
U(I+1)=-U(I+1)
V(I+1)=-V(I+1)
22 CONTINUE
21 IF(NN.EQ.1) GO TO 23
N1=N+1
DO 24 I=1,N1
V(I)=-V(I)
24 CONTINUE
23 RETURN
END
FUNCTION COSH(X)
COSH=(EXP(X)+EXP(-X))/2.0
RETURN
END
FUNCTION SINH(X)
SINH=(EXP(X)-EXP(-X))/2.0
RETURN
END

```

C DATA CARDS
C VARIABLE

FORMAT

```

C   COORDINATES (X,Y,Z)           3F10.0
C   A,B,C                         3F10.0
C   M1,M2                         2I4
C   LMIN,LMAX,LSTEP              3F10.0
C   K,L                           2I4
C   VALUES OF U(J)              F10.0
C   VALUES OF F(J)              F10.0
C   WATES DATA IN SETS OF THREE CARDS
C   M0,M1,M2                      3I4
C   T                             F10.0
C   IL,OL                        2I4
C   END OF WATES DATA MARKED BY M0,M1,M2 =      0      0      0
C   MORE                          I4
C   IF MORE > 0 READ NEW DATA, OTHERWISE STOP
C   NEW VALUES OF LMIN,LMAX,LSTEP
C   SET OF WATES DATA (AS ABOVE)
C   MORE
C   ANOTHER CONTROL CARD MORE
C   ETC
*****

```

#LISTING OF :GEOL.ANDY3(1/) PRODUCED ON 15JAN74 AT 23.24.10
#OUTPUT BY LISTFILE IN ' :GEOL.MORCMS' ON 15JAN74 AT 23.35.48
DOCUMENT ANDY3

```

C **** PROGRAM ORTHO ****
PROGRAM ORTHO(INPUT,OUTPUT,TAPE 5=INPUT,TAPE 6=OUTPUT)
REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9)
1,K,KPR
DIMENSION TABA(9,75),TABD(9),TAPE(9)
1,TABF(75,100)
C COMMON BLOCK DATA PASSES DATA
COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
C COMMON BLOCK VALS PASSES RESULTS
COMMON/VALS/TABA,TABB,TABC,TABD,TABE
C COMMON BLOCK FRES PASSES RESULTS FROM TABLEF
COMMON /FRES/TABF
LEVEL 2,TABF
CALL INPUT
GO TO 101
100 CALL NEWD
WRITE(6,6008)
6008 FORMAT(2H1 //12H NEWD CALLED//)
101 CONTINUE
C OUTPUT DATA
WRITE(6,6006)A,B,C,M1,M2,KMIN,KMAX,KSTEP,KR,LR
6006 FORMAT(//12H DATA GIVEN //3H A=,F10.4,5X,
13H B=,F10.4,5X,3H C=,F10.4//4H M1=,I4,
25X,4H M2=,I4,5X//6H KMIN=,F10.4,5X
3,6H KMAX=,F10.4,7H KSTEP=,F10.4//
44H KR=,I4,5X,4H LR=,I4)
WRITE(6,6004)
6004 FORMAT(///23H VALUES OF COORDINATES /15X,2H X,9X,2H Y,8X,2H Z/)
DO 57 J=1,9
WRITE(6,6005)J,(COORDS(J,I),I=1,3)
57 CONTINUE
6005 FORMAT(3H J=,I2,5X,3F10.4)
WRITE(6,6003)
6003 FORMAT(///22H VALUES OF UJ AND FJ //12X,
120H UJ FJ /)
WRITE(6,6007)((J,UJ(J),FJ(J)),J=1,9)
6007 FORMAT(3H J=,I2,5X,2F10.4)
C SET VALUE OF K
K=KMIN
CALL TABLEA
C SET UP LOOP FOR STEPS IN K
DO 30 KC=1,100
C SET UP LOOP FOR NUMBER OF LAYERS
DO 20 MC=M1,M2
C CALCULATE VALUE OFP(M)
IPM=5*MC
FIPM=FLOAT(IPM)
C SET UP LOOP FOR ATOMS J
DO 10 J=1,9
C IFUJ = ZERO SKIP UNNECESSARY CALCULATIONS
IF(UJ(J))14,14,1
1 CONTINUE
C AVOID UNNECESSARY CALCULATIONS FOR ATOMS WITH THE SAME X COORDINATES
GO TO (11,11,11,11,12,11,12,11,12),J
11 CALL TABLEB(J,K,MC,FIPM)

```

```

      CALL TABLEC(IPM)
12    CALL TABLED(J,MC)
      GO TO 10
14    TABD(J)=0,0
      TABE(J)=0,0
10    CONTINUE
      CALL TABLEF(MC,KC)
20    CONTINUE
C INCREMENT K
      K=K+KSTEP
      IF(K.GT,KMAX) GO TO 13
30    CONTINUE
C SET KOUNT TO KC, THE NUMBER OF STEPS OF K
13    KOUNT=KC
C OUTPUT SAMPLE RESULTS FROM TABLE
      WRITE(6,6000)
6000  FORMAT(2H1 ,45X,10H TABLES F /)
      M1A2=M1+2
      DO 45 MCC=M1,M1A2
      WRITE(6,6002)MCC
6002  FORMAT(/3H M=,I4)
      KPR=KMIN
      DO 45 KCC=1,KOUNT
      WRITE(6,6001)KPR,TABF(MCC,KCC)
6001  FORMAT(3H K=,F7.4,5X,F10.4)
      KPR=KPR+KSTEP
      K=K+KSTEP
45    CONTINUE
      CALL WATES(KOUNT)
C MORE IS A PROGRAM CONTROL
      READ(5,5000)MORE
5000  FORMAT(I4)
      IF(MORE)9,9,100
C IF MORE > ZERO CALL NEWD
9     CONTINUE
      STOP
      END

```

```

      SUBROUTINE INPUT
C READS IN DATA
      REAL COORDS(9,3),KMIN,KMAX,UJ(9),FJ(9),KSTEP
      COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
      READ(5,5000)((COORDS(I,J),J=1,3),I=1,9)
5000  FORMAT(3F10.0)
5001  FORMAT(F10.0)
      READ(5,5000)A,B,C
      READ(5,5002)M1,M2
5002  FORMAT(2I4)
      READ(5,5000)KMIN,KMAX,KSTEP
      READ(5,5002)KR,LR
      READ(5,5001)(UJ(I),I=1,9)
      READ(5,5001)(FJ(I),I=1,9)
      WRITE(6,6000)
6000  FORMAT(/,20H1INPUT SUCCESSFUL )
      RETURN
      END

```

```

      SUBROUTINE TABLEA
C CALCULATE B(M,J)/B
      REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9)

```

```

        DIMENSION TABA(9,75),TARD(9),TARE(9)
        COMMON/ DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
        COMMON/ VALS/TABA,TABB,TABC,TARD,TARE
        DO 14 J=1,9
C IF UJ = ZERO AVOID UNNECESSARY CALCULATIONS
        IF(UJ(J))8,14,8
        8   CONTINUE
C AVOID CALCULATIONS FOR THE J TH ATOM WITH THE SAME X COORDINATES
C AS THE J-1 TH ATOM
        GO TO (11,11,11,11,12,11,12,11,12), J
        11  CONTINUE
        DO 10 I= M1,M2
        FI=FLOAT(I)
C ASSIGN VALUES FOR THE J TH ATOM IN THE I TH LAYER
        TABA(J,I)=(FI+COORDS(J,I))/FI
        10  CONTINUE
        GO TO 14
        12  CONTINUE
        DO 13 I=M1,M2
        TABA(J,I)=TABA(J-1,I)
        13  CONTINUE
        14  CONTINUE
        RETURN
        END

```

```

        SUBROUTINE TABLEB(J,K,MC,FIPM)
C CALCULATE P(M)*(B(M,J)/B)*K
        REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9),K
        DIMENSION TABA(9,75),TARD(9),TARE(9)
        COMMON/ DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
        COMMON/ VALS/TABA,TABB,TABC,TARD,TARE
        TABB=FIPM*TABA(J,MC)*K
        RETURN
        END

```

```

        SUBROUTINE TABLEC(IPM)
        REAL KMIN,KMAX,KSTEP,K,UJ(9),FJ(9),COORDS(9,3),
        1BFLIB(2000),BFLIB2(2000)
        DIMENSION TABA(9,75),TARD(9),TARE(9)
        COMMON/ DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
        COMMON/ VALS/TABA,TABB,TABC,TARD,TARE
        X=0.0
        IR=IPM*KR
C CALL BESSJO IF IR = ZERO
        IF(IR.EQ.0) GO TO 13
C IR IS THE ORDER OF THE BESSEL FUNCTION REQUIRED
        CALL BESSJN(TABB,X,BFLIB,BFLIB2,IR)
C BFLIB(IR+1) CONTAINS THE VALUE OF BESSEL FUNCTION OF ORDER IR
        TABC=BFLIB(IR+1)
        GO TO 20
        13  CONTINUE
        CALL BESSJO(TABB,X,BF1,BF2)
        TABC=BF1
        20  CONTINUE
        RETURN
        END

```

```

SUBROUTINE TABLED(J,MC)
  REAL KMIN,KMAX,UJ(9),FJ(9),K,KSTEP,
  1TD1(9),TD2(9),TD3(9),TD4(9),TD5(9),TD6(9)
  2,COORDS(9,3)
  DIMENSION TABA(9,75),TARD(9),TARE(9)
  COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
  COMMON/VALS/TABA,TABB,TABC,TABD,TABE
C TD1 ETC ARE CONSTANT FOR A GIVEN VALUE OF J AT ANY VALUE OF M; THEY
C ARE THEREFORE CALCULATED ONLY ONCE FOR EACH VALUE OF J
  IF(MC.GT,M1) GO TO 10
  FLR=FLOAT(LR)
  FKR=FLOAT(KR)
  TD1(J)=UJ(J)*FJ(J)
  TD2(J)=COS(6.2832*FKR*COORDS(J,2))
  TD3(J)=COS(6.2832*FLR*COORDS(J,3))
  TD4(J)=SIN(6.2832*FLR*COORDS(J,3))
  TD5(J)=TD1(J)*TD2(J)*TD3(J)
  TD6(J)=TD1(J)*TD2(J)*TD4(J)
  10 TABD(J)=TABC*TD5(J)
  TABE(J)=TABC*TD6(J)
  RETURN
  END

```

```

SUBROUTINE TABLEF(MC,KC)
C SUM CONTRIBUTIONS FROM ALL J ATOMS IN EACH LAYER
  REAL KMIN,KMAX,KSTEP,K,UJ(9),FJ(9),COORDS(9,3)
  DIMENSION TABA(9,75),TARD(9),TARE(9),TABF(75,100)
  COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
  COMMON/VALS/TABA,TABB,TABC,TABD,TABE
  COMMON/FRES/TABF
  LEVEL 2,TABF
C SET TF1,TF2
  TF1=0.0
  TF2=0.0
C SUM OVER J ATOMS
  DO 10 J=1,9
    TF1=TF1+TABD(J)
    TF2=TF2+TABE(J)
  10 CONTINUE
C SQUARE THE SUMS
  TF1=TF1*TF1
  TF2=TF2*TF2
C ADD THE SQUARES
  TABF(MC,KC)=TF1+TF2
  RETURN
  END

```

```

SUBROUTINE NEWD
C COLLECT NEW RANGE OF K
  REAL KMIN,KMAX,KSTEP,UJ(9),FJ(9),COORDS(9,3)
  COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
  READ(5,5002)KMIN,KMAX,KSTEP
  5002 FORMAT(3F10.0)
  RETURN
  END

```

SUBROUTINE WATES(KOUNT)

```

C APPLY WEIGHTS TO RESULTS FROM TABLE
  REAL KMIN,KMAX,KSTEP,UJ(9),FJ(9),COORDS(9,3)
  DIMENSION TABF(75,100),V(75),WF(75),IPMSQ(75),RES(100)
  COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
  COMMON/FRES/TABF
  LEVEL 2,TABF
C HEADING
  WRITE(6,6000)
6000 FORMAT(///20H RESULTS FROM WATES //)
5000 FORMAT(3I4)
5001 FORMAT(F10.0)
  DO 10 I=M1,M2
    IPMSQ(I)=(I*5)**2
  10 CONTINUE
  20 READ(5,5000)M0,MW1,MW2
C IF M0<= ZERO RETURN TO MAIN PROGRAM
  IF(M0)14,14,11
  11 READ(5,5001)T
  FM0=FLOAT(M0)
C CALCULATE THE WEIGHTS
  R=1.0/FM0
  DO 12 I=MW1,MW2
    FI=FLOAT(I)
    X=((1.0/FI)*R)**2)*T*FI
    IF (X.EQ.0.0) GO TO 13
    Y(I)=EXP(-X)
    GO TO 12
  13 Y(I)=1.0
  12 CONTINUE
C SET WEIGHT OF NEUTRAL LAYER TO ONE
  WF(M0)=1.0
  I=M0+1
  MW2S1= MW2-1
  DO 70 J=M0,MW2S1
    WF(I)=WF(I-1)*Y(I)
  70 CONTINUE
C WEIGHT FOR THE I TH LAYER IS IN WF(I)
  I=I+1
  70 CONTINUE
  I=M0-1
  MOS1=M0-1
  DO 71 J=MW1,MOS1
    WF(I)=WF(I+1)*Y(I)
    I=I-1
  71 CONTINUE
  DO 15 L=1,KOUNT
    AW=0.0
C APPLY WEIGHTS AND SUM CONTRIBUTIONS FROM REQUIRED LAYERS;RESULT IN AW
    DO 16 MC=MW1,MW2
      F=FLOAT(IPMSQ(MC))
      BW=TABF(MC,L)*F*WF(MC)
      AW=AW+BW
    16 CONTINUE
C PUT RESULT OF SUMMATION INTO RES(L)
    RES(L)=AW
  15 CONTINUE
C OUTPUT RESULTS
  WRITE(6,6001)KR,LR,MW1,MW2,M0,T
C HEADINGS
6001 FORMAT(/25H PROFILE OF REFLECTION 0,I1,I1/
17H LAYERS,I4,3H TO,I4,11H CONSIDERED/
216H NEUTRAL LAYER =,I3,5X,4H T =,F8.2/)
  RL=KMIN
  DO 19 L=1,KOUNT
    WRITE(6,6002)RL,RES(L)
  19 CONTINUE
6002 FORMAT(3H K=,F7.4,5X,F15.4)
  RL=RL+KSTEP

```

```

19  CONTINUE
    GO TO 20
14  CONTINUE
    RETURN
    END

```

```

SUBROUTINE BESSJO(X,PHI,U0,V0)
C OXLIB 1900 LIBRARY PROGRAM
  IF(X,NE,0,0) GO TO 10
  U0=1,0
  V0=0,0
  RETURN
10  N=1
  IF(PHI,LT,0,0) N=-1
  ARG=ABS(PHI)
  IF(ARG,GE,3.14159265358979) ARG=ARG-3.14159265358979
  IF(X,GE,10,0) GO TO 11
  X1=X/2,0
  ZARG=ARG+ARG
  FAC=1,0
  DO 21 K=1,100
  FAC=FAC*X1/FLOAT(K)
  IF(ABS(FAC),LT,1,0E-10) GO TO 25
21  CONTINUE
  K=100
25  FK=FLOAT(K)
  U0=FAC*FAC*COS(FK*ZARG)
  V0=FAC*FAC*SIN(FK*ZARG)
  J=MOD(K,2)
  IF(J,EQ,0) GO TO 26
  U0=-U0
  V0=-V0
26  M=K
  DO 22 L=2,M
  K=K-1
  FAX=FAC*FLOAT(K+1)/X1
  FAX=FAC*FAC
  IF(J,EQ,0) GO TO 23
  FAX=-FAX
23  FK=FLOAT(K)
  U0=U0+FAX*COS(FK*ZARG)
  V0=V0+FAX*SIN(FK*ZARG)
22  CONTINUE
  U0=U0+1,0
  GO TO 12
11  C=SQRT(2,0/(X*3.14159265358979))
  A=C*COS(ARG/2,0)
  B=C*SIN(ARG/2,0)
  C=COS(-3.14159265358979/4,0)
  S=SIN(-3.14159265358979/4,0)
  CA=COS(ARG)*X
  SA=SIN(ARG)*X
  CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
  CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S
  SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
  SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
  P=(5,0*3,0)/(2,0*2,0**6,0*X**2,0)
  Q=1,0/(2,0*2,0**6,0*X**2,0)
  P1=P
  Q1=Q
  DO 1 K=2,100
  P=P*(FLOAT(4*K-1)*FLOAT(4*K-1)*FLOAT(4*K-3)*FLOAT(4*K-3))/
1 (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))

```

```

      Q=Q*(FLOAT(4*K-3)*FLOAT(4*K-3)*FLOAT(4*K-5)*FLOAT(4*K-5))/
1 (FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
      IF((P.LT.1.0E-10).AND.(Q.LT.1.0E-10)) GO TO 2
      IF((P.LE.P1).AND.(Q.LE.Q1)) GO TO 8
      P=P1
      Q=Q1
      GO TO 9
8  P1=P
   Q1=Q
1  CONTINUE
   K=100
   GO TO 2
9  K=K-1
2  Q=Q*FLOAT(2*K)*FLOAT(2**3)*X
   J=MOD(K,2)
   IF(J.EQ.0) GO TO 3
   I=-1
   GO TO 4
3  I=1
4  FI=FLOAT(I)
   FK=FLOAT(K)
   PR=FI*P*COS(2.0*FK*ARG)
   PI=-FI*P*SIN(2.0*FK*ARG)
   QR=FI*Q*COS(2.0*FK*ARG-ARG)
   QI=-FI*Q*SIN(2.0*FK*ARG-ARG)
   M=K
   DO 5 L=2,M
      K=K-1
      P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4*K+3)*FLOAT(4*K+3)*FLOAT(4*K+1)*FLOAT(4*K+1))
      Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4*K+1)*FLOAT(4*K+1)*FLOAT(4*K-1)*FLOAT(4*K-1))
      J=MOD(K,2)
      IF(J.EQ.0) GO TO 6
      I=-1
      GO TO 7
6  I=1
7  FI=FLOAT(I)
   FK=FLOAT(K)
   PR=PR+FI*P*COS(2.0*FK*ARG)
   PI=PI+FI*P*SIN(2.0*FK*ARG)
   QR=QR+FI*Q*COS(2.0*FK*ARG-ARG)
   QI=QI+FI*Q*SIN(2.0*FK*ARG-ARG)
5  CONTINUE
   PR=PR+1.0
   U0=A*(PR*CR-PI*CI-QR*SR+QI*SI)-B*(PI*CR+PR*CI-QI*SR-QR*SI)
   V0=A*(PI*CR+PR*CI-QI*SR-QR*SI)+B*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(N.EQ.1) GO TO 13
   V0=-V0
13 RETURN
   END

```

```

      SUBROUTINE BESSJ1(X,PHI,U1,V1)
C OXLIB 1900 LIBRARY PROGRAM
      IF(X.NE.0.0) GO TO 10
      U1=0.0
      V1=0.0
      RETURN
10  N=1
      IF(PHI.LT.0.0) N=-1
      ARG=ABS(PHI)
      IF(ARG.GE.3.14159265358979) ARG=ARG-3.14159265358979
      IF(X.GE.10.0) GO TO 11

```

```

X1=X/2;S=
ZARG=ARG+ARG
A=COS (ARG)
B=SIN (ARG)
FAC=1,0
DO 21 K=1,100
FAC=FAC*X1/FLOAT(K)
IF(ABS(FAC).LT,1.0E-10) GO TO 25
21 CONTINUE
K=100
25 FK=FLOAT(K)
U0=FAC*FAC*FLOAT(K)*COS(FK*ZARG)
V0=FAC*FAC*FLOAT(K)*SIN(FK*ZARG)
J=MOD(K,2)
IF(J.EQ,0) GO TO 26
U0=-U0
V0=-V0
26 M=K
DO 22 L=2,M
K=K+1
FAC=FAC*FLOAT(K+1)/X1
FAX=FAC*FAC
J=MOD(K,2)
IF(J.EQ,0) GO TO 23
FAX=-FAX
23 FK=FLOAT(K)
U0=U0+FAX*FLOAT(K)*COS(FK*ZARG)
V0=V0+FAX*FK*SIN(FK*ZARG)
22 CONTINUE
U0=U0/X1
V0=V0/X1
U1=-(U0*A+V0*B)
V1=U0*B-V0*A
GO TO 12
11 C=SQRT(2,0/(X*3,14159265358979))
A=C*COS(ARG/2,0)
B=C*SIN(ARG/2,0)
C=COS(-3,14159265358979*0,75)
S=SIN(-3,14159265358979*0,75)
CA=COS(ARG)*X
SA=SIN(ARG)*X
CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S
SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
P=3,0*5,0/(2,0*2,0**6,0*X**2,0)
Q=3,0/(2,0*2,0**6,0*X**2,0)
P1=P
Q1=Q
DO 1 K=2,100
P=P*FLOAT(4-(4*K-1)*(4*K-1))*FLOAT(4-(4*K-3)*(4*K-3))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
Q=Q*FLOAT(4-(4*K-3)*(4*K-3))*FLOAT(4-(4*K-5)*(4*K-5))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
IF((P.LT,1.0E-10).AND.(Q.LT,1.0E-10)) GO TO 2
IF((P.LE,P1).AND.(Q.LE,Q1)) GO TO 8
P=P1
Q=Q1
GO TO 9
8 P1=P
Q1=Q
1 CONTINUE
K=100
GO TO 2
9 K=K+1
2 Q=Q*FLOAT(2*K)*FLOAT(2**3)*X

```

```

J=MOD(K,2)
IF(J.EQ.0) GO TO 3
I=1
GO TO 4
3 I=1
4 FI=FLOAT(I)
FK=FLOAT(K)
PR=FI*P*COS(2.0*FK*ARG)
PI=-FI*P*SIN(2.0*FK*ARG)
QR=FI*Q*COS(2.0*FK*ARG-ARG)
QI=-FI*Q*SIN(2.0*FK*ARG-ARG)
M=K
DO 5 L=2,M
K=K+1
P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
1(FLOAT(4-(4*K+3)*(4*K+3))*FLOAT(4-(4*K+1)*(4*K+1)))
Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
1(FLOAT(4-(4*K+1)*(4*K+1))*FLOAT(4-(4*K-1)*(4*K-1)))
J=MOD(K,2)
IF(J.EQ.0) GO TO 6
I=1
GO TO 7
6 I=1
7 FI=FLOAT(I)
FK=FLOAT(K)
PR=PR+FI*P*COS(2.0*FK*ARG)
PI=PI+FI*P*SIN(2.0*FK*ARG)
QR=QR+FI*Q*COS(2.0*FK*ARG-ARG)
QI=QI+FI*Q*SIN(2.0*FK*ARG-ARG)
5 CONTINUE
PR=PR+1.0
U1=A*(PR*CR-PI*CI-QR*SR+QI*SI)-B*(PI*CR+PR*CI-QI*SR-QR*SI)
V1=A*(PI*CR+PR*CI-QI*SR-QR*SI)+B*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(ABS(PHI).LT.3.14159265358979) GO TO 13
U1=U1
V1=V1
13 IF(N.EQ.-1) V1=-V1
RETURN
END

```

```

SUBROUTINE BESSJN(X,PHI,U,V,N)
C OXLIB 1900 LIBRARY PROGRAM
DIMENSION U(2),V(2)
IF(X.NE.0.0) GO TO 30
U(1)=1.0
V(1)=0.0
DO 31 I=1,N
U(I+1)=0.0
V(I+1)=0.0
31 CONTINUE
RETURN
30 NN=1
IF(PHI.LT.0.0) NN=-1
ARG=ABS(PHI)
IF(ARG.GE.3.14159265358979) ARG=ARG-3.14159265358979
FN=FLOAT(N)
IF(X.LE.FN) GO TO 1
CALL BESSJ0(X,ARG,U(1),V(1))
IF(N.LT.1) GO TO 20
CALL BESSJ1(X,ARG,U(2),V(2))
IF(N.LT.2) GO TO 20
DO 10 I=2,N
U(I+1)=(2.0*FLOAT(I-1)*U(I)*COS(ARG)+2.0*FLOAT(I-1)*V(I)*

```

```

1 SIN (ARG))/X=U(I-1)
V(I+1)=(2.0*FLOAT(I-1)*V(I)*COS (ARG)-2.0*FLOAT(I-1)*U(I)*
1 SIN (ARG))/X=V(I-1)
10 CONTINUE
GO TO 20
1 N1=N+1
IX=IFIX(X)
K=IX+20
IF(K,LT,N) K=N
2 SCAR=1000000.0
SCAI=1000000.0
STRR=0.0000001
STRI=0.0000001
WAR=STRR
WAI=STRI
WBR=0.0
WBI=0.0
J=K+1
DO 3 I=1,K
J=J-1
WCR=(2.0*FLOAT(J)*WAR*COS (ARG)+2.0*FLOAT(J)*WAI*SIN (ARG))/X-WBR
WCI=(2.0*FLOAT(J)*WAI*COS (ARG)-2.0*FLOAT(J)*WAR*SIN (ARG))/X-WBI
WBR=WAR
WBI=WAI
WAR=WCR
WAI=WCI
IF((J-1),GT,N) GO TO 4
U(J)=WCR
V(J)=WCI
4 IF((ABS(WCR),LE,SCAR).AND.(ABS(WCI),LE,SCAI)) GO TO 3
WAR=WAR/SCAR
WBR=WBR/SCAR
STRR=STRR/SCAR
IF(J,GT,N1) GO TO 8
DO 6 L=J,N1
U(L)=U(L)/SCAR
6 CONTINUE
8 CONTINUE
WAI=WAI/SCAI
WBI=WBI/SCAI
STRI=STRI/SCAI
IF(J,GT,N1) GO TO 3
DO 9 L=J,N1
V(L)=V(L)/SCAI
9 CONTINUE
3 CONTINUE
CALL BESSJO(X,ARG,UL,VL)
ULAM=(UL*U(1)+VL*V(1))/(U(1)**2+V(1)**2)
VLAM=(VL*U(1)-UL*V(1))/(U(1)**2+V(1)**2)
IF((ABS (STRR*ULAM),LE,0.00000000001).AND.(ABS (STRI*VLAM),LE,
10.00000000001)) GO TO 5
K=K+10
GO TO 2
5 DO 7 L=1,N1
UU=U(L)
VV=V(L)
U(L)=UU*ULAM-VV*VLAM
V(L)=VV*ULAM+UU*VLAM
7 CONTINUE
20 IF(ABS(PHI),LT,3.14159265358979) GO TO 21
DO 22 I=1,N
K=MOD(I,2)
IF(K,EQ,0) GO TO 22
U(I+1)=-U(I+1)
V(I+1)=-V(I+1)
22 CONTINUE

```

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[illegible]

#LISTING OF 1GEOL.ANDY4(1/) PRODUCED ON 14JAN74 AT 22.58.36

#OUTPUT BY LISTFILE IN 'GEOLOG.MOPCMS' ON 14JAN74 AT 23.07.10

DOCUMENT ANDY4

```

C**** PROGRAM ORTHOH ****
      PROGRAM ORTHOH(INPUT,OUTPUT,TAPE 5=INPUT,TAPE 6= OUTPUT)
      REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9)
      1,K,KPR
      DIMENSION TABA(9,75),TABD(9),TARE(9)
      1,TABF(75,100),TABD2(9),TARE2(9)
C COMMON BLOCK DATA PASSES DATA
      COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
C COMMON BLOCK VALS PASSES RESULTS
      COMMON/VALS/TABA,TABB,TABC,TABD,TABF
C COMMON BLOCK FRES PASSES RESULTS FROM TABLE
      COMMON /FRES/TABF
C COMMON BLOCK CDH PASSES RESULTS
      COMMON/CDH/TABC2,TABD2,TARE2
      LEVEL 2,TABF
      CALL INPUT(RN)
C RN IS THE ORDER OF THE HELIX
      GO TO 101
100  CALL NEWD(RN)
      WRITE(6,6008)
6008  FORMAT(2H1 ,//12H NEWD CALLED//)
101  CONTINUE
C OUTPUT DATA
      WRITE(6,6006)A,B,C,M1,M2,KMIN,KMAX,KSTEP,KR,LR
6006  FORMAT(//12H DATA GIVEN //3H A=,F10.4,5X,
13H B=,F10.4,5X,3H C=,F10.4//4H M1=,14,
25X,4H M2=,14,5X//6H KMIN=,F10.4,5X
3,6H KMAX=,F10.4,7H KSTEP=,F10.4//
44H KR=,14,5X,4H LR=,14)
      WRITE (6,6004)
6004  FORMAT(///23H VALUES OF COORDINATES /15X,2H X,9X,2H Y,8X,2H Z/)
      DO 57 J=1,9
      WRITE(6,6005)J,(COORDS(J,I),I=1,3)
57  CONTINUE
6005  FORMAT(3H J=,12,5X,3F10.4)
      WRITE(6,6003)
6003  FORMAT(///22H VALUES OF UJ AND FJ //12X,
120H          UJ          FJ      /)
      WRITE(6,6007)((J,UJ(J),FJ(J)),J=1,9)
6007  FORMAT(3H J=,12,5X,2F10.4)
      WRITE(6,6009)RN
6009  FORMAT(/20H ORDER OF HELIX IS ,F5.2)
      FLR=FLOAT(LR)
      RN=RN*FLR
C SET K
      K=KMIN
      CALL TABLEA
C SET UP LOOP FOR STEPS IN K
      DO 30 KC=1,100
C SET UP LOOP FOR NUMBER OF LAYERS
      DO 20 MC=M1,M2
C CALCULATE VALUE OFP(M)
      IPM=5*MC
      FIPM=FLOAT(IPM)
      U=1.00
      F=1.00
      F=1.00

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```

C SET UP LOOP FOR ATOMS J
DO 10 J=1,9
C IF UJ = ZERO SKIP UNNECESSARY CALCULATIONS
IF(UJ(J))14,14,1
1 CONTINUE
C AVOID UNNECESSARY CALCULATIONS FOR ATOMS WITH THE SAME X COORDINATES
GO TO (11,11,11,11,12,11,12,11,12),J
11 CALL TABLEB(J,K,MC,FIPM)
CALL TABLEC(1PM,RN)
12 CALL TABLED(J,MC)
GO TO 10
14 TABD(J)=0,0
TABE(J)=0,0
TABDZ(J)=0,0
TABEZ(J)=0,0
10 CONTINUE
CALL TABLEF(MC,KC)
20 CONTINUE
C INCREMENT K
K=K+KSTEP
IF(K,GT,KMAX) GO TO 13
30 CONTINUE
C SET KOUNT = KC, THE NUMBER OF STEPS IN K
13 KOUNT=KC
C OUTPUT SAMPLE RESULTS FROM TABLEF
WRITE(6,6000)
6000 FORMAT(2H1,45X,10H TABLES F /)
M1A2=M1+2
DO 45 MCC=M1,M1A2
WRITE(6,6002)MCC
6002 FORMAT(/3H M=,I4)
KPR=KMIN
DO 45 KCC=1,KOUNT
WRITE(6,6001)KPR,TABF(MCC,KCC)
6001 FORMAT(3H K=,F7.4,5X,F10.4)
KPR=KPR+KSTEP
K=K+KSTEP
45 CONTINUE
CALL WATES(KOUNT)
C MORE IS A PROGRAM CONTROL
READ(5,5000)MORE
5000 FORMAT(I4)
C IF MORE > ZERO CALL NEWD
IF(MORE)9,9,100
9 CONTINUE
STOP
END
SUBROUTINE INPUT(RN)
C READS IN DATA
REAL COORDS(9,3),KMIN,KMAX,UJ(9),FJ(9),KSTEP
COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
READ(5,5000)((COORDS(I,J),J=1,3),I=1,9)
5000 FORMAT(3F10,0)
5001 FORMAT(F10,0)
READ(5,5000)A,B,C
READ(5,5002)M1,M2
5002 FORMAT(2I4)
READ(5,5000)KMIN,KMAX,KSTEP
READ(5,5002)KR,LR
READ(5,5001)(UJ(I),I=1,9)
READ(5,5001)(FJ(I),I=1,9)
READ(5,5003)RN
5003 FORMAT(F10,0)
WRITE(6,6000)
6000 FORMAT(/20H1 INPUT SUCCESSFUL )
RETURN

```

```

END
SUBROUTINE TABLEA
C CALCULATE B(M,J)/R
REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9)
DIMENSION TABA(9,75),TABD(9),TABE(9)
COMMON/ DATA/ COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
COMMON/ VALS/ TABA,TABB,TABC,TABD,TABE
DO 14 J=1,9
C IF UJ = ZERO AVOID UNNECESSARY CALCULATIONS
IF(UJ(J))8,14,8
X CONTINUE
C AVOID CALCULATIONS FOR THE J TH ATOM WITH THE SAME X COORDINATES
C AS THE J-1 TH ATOM
GO TO (11,11,11,11,12,11,12,11,12), J
11 CONTINUE
DO 10 I= M1,M2
FI=FLOAT(I)
C ASSIGN VALUES FOR THE J TH ATOM IN THE I TH LAYER
TABA(J,I)=(FI+COORDS(J,1))/FI
10 CONTINUE
GO TO 14
12 CONTINUE
DO 13 I=M1,M2
TABA(J,I)=TABA(J-1,I)
13 CONTINUE
14 CONTINUE
RETURN
END
SUBROUTINE TABLEB(J,K,MC,FIPM)
C CALCULATE P(M)*(B(M,J)/B)*K
REAL COORDS(9,3),KMIN,KMAX,KSTEP,UJ(9),FJ(9),K
DIMENSION TABA(9,75),TABD(9),TABE(9)
COMMON/ DATA/ COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
COMMON/ VALS/ TABA,TABB,TABC,TABD,TABE
TABB=FIPM*TABA(J,MC)*K
RETURN
END
SUBROUTINE TABLEC(IPM,RN)
REAL KMIN,KMAX,KSTEP,K,UJ(9),FJ(9),COORDS(9,3),
1BFLIB(2000),BFLIB2(2000),SBF(2000),SBF2(2000),
2TABD2(9),TABE2(9)
DIMENSION TABA(9,75),TABD(9),TABE(9)
COMMON/ DATA/ COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
COMMON/ VALS/ TABA,TABB,TABC,TABD,TABE
COMMON/ CDH/ TABC2,TABD2,TABE2
X=0,0
IR=IPM*KR
FIR=FLOAT(IR)
F2=FIR-RN
C 0.001 ADDED TO MAKE VALUE F.G. 25.001 RATHER THAN 24.9999999
F2=F2+0.0001
IRH2=IFIX(F2)
C 0.001 ADDED TO MAKE VALUE F.G. 25.001 RATHER THAN 24.9999999
RN2=RN+0.0001
IRN=IFIX(RN2)
IRH=IR+IRN
FIRN=FLOAT(IRN)
C TEST WHETHER THE ORDERS ARE INTEGRAL OR HALF-INTEGRAL
D=RN-FIRN
IF(D.GT,0.4) GO TO 10
C IR+RN AND IR-RN ARE THE ORDERS OF THE BESSEL FUNCTIONS REQUIRED
C PROCEDURE FOR INTEGRAL ORDERS
CALL BESSJN(TABB,X,BFLIB,BFLIB2,IRH)
C BFLIB(X+1) CONTAINS THE VALUE OF THE BESSEL FUNCTION OF ORDER X
TABC=BFLIB(IRH+1)
TABC2=BFLIB(IRH2+1)

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      GO TO 11
10  CONTINUE
C  PROCEDURE FOR HALF-INTEGRAL ORDERS
      CALL SPHEJN(TABB,SBF,SBF2,IRH)
C  SBF(X+1) CONTAINS THE VALUE OF THE BESSEL FUNCTION OF ORDER X
      TABC=SBF(IRH+1)/(SQRT(1.5708/TABB))
      TABC2=SBF(IRH2+1)/(SQRT(1.5708/TABB))
11  CONTINUE
      RETURN
      END
      SUBROUTINE TABLED(J,MC)
      REAL KMIN,KMAX,UJ(9),FJ(9),K,KSTEP,
      1TD1(9),TD2(9),TD3(9),TD4(9),TD5(9),TD6(9)
      2,COORDS(9,3)
      DIMENSION TABA(9,75),TARD(9),TARE(9)
      1,TABD2(9),TAFE2(9)
      COMMON/ DATA/ COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
      COMMON/ VALS/ TABA,TABB,TABC,TARD,TABF
      COMMON/ CDH/ TABC2,TABD2,TAFE2
C  TD1 ETC ARE CONSTANT FOR A GIVEN VALUE OF J AT ANY VALUE OF M; THEY
C  ARE THEREFORE CALCULATED ONLY ONCE FOR EACH VALUE OF J
      IF(MC,GT,M1) GO TO 10
      FLR=FLOAT(LR)
      FKR=FLOAT(KR)
      TD1(J)=UJ(J)*FJ(J)
      TD2(J)=COS(6.2832*FKR*COORDS(J,2))
      TD3(J)=COS(6.2832*FLR*COORDS(J,3))
      TD4(J)=SIN(6.2832*FLR*COORDS(J,3))
      TD5(J)=TD1(J)*TD2(J)*TD3(J)
      TD6(J)=TD1(J)*TD2(J)*TD4(J)
10  TABD(J)=TABC*TD5(J)
      TABD2(J)=TABC2*TD5(J)
      TAFE(J)=TABC*TD6(J)
      TAFE2(J)=TABC2*TD6(J)
      RETURN
      END
      SUBROUTINE TABLEF(MC,KC)
C  SUM CONTRIBUTIONS FROM ALL J ATOMS IN EACH LAYER
      REAL KMIN,KMAX,KSTEP,K,UJ(9),FJ(9),COORDS(9,3)
      DIMENSION TABA(9,75),TARD(9),TARE(9),TABF(75,100)
      1,TABD2(9),TAFE2(9)
      COMMON/ CDH/ TABC2,TABD2,TAFE2
      COMMON/ DATA/ COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
      COMMON/ VALS/ TABA,TABB,TABC,TABD,TABE
      COMMON/ PRES/ TABF
      LEVEL 2,TABF
C  SET TF1,TF2,TF1H,TF2H
      TF1=0.0
      TF2=0.0
      TF1H=0.0
      TF2H=0.0
C  SUM OVER J ATOMS
      DO 10 J=1,9
      TF1=TF1+TABD(J)
      TF2=TF2+TAFE(J)
      TF1H=TF1H+TABD2(J)
      TF2H=TF2H+TAFE2(J)
10  CONTINUE
C  SQUARE THE SUMS
      TF1=TF1*TF1
      TF2=TF2*TF2
      TF1H=TF1H*TF1H
      TF2H=TF2H*TF2H
C  ADD THE SQUARES
      TABF(MC,KC)=TF2+TF1+TF2H+TF1H
      RETURN

```

```

END
SUBROUTINE NEWD(RN)
C READ NEW RANGE OF K AND NEW VALUE OF RN
REAL KMIN,KMAX,KSTEP,UJ(9),FJ(9),COORDS(9,3)
COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
READ(5,5002)KMIN,KMAX,KSTEP
5002 FORMAT(3F10,0)
READ(5,5000)RN
5000 FORMAT(F10,0)
RETURN
END
SUBROUTINE WATES(KOUNT)
C APPLY WEIGHTS TO RESULTS FROM TABLE
REAL KMIN,KMAX,KSTEP,UJ(9),FJ(9),COORDS(9,3)
DIMENSION TABF(75,100),Y(75),WF(75),IPMSQ(75),RES(100)
COMMON/DATA/COORDS,A,B,C,M1,M2,KMIN,KMAX,KR,LR,UJ,FJ,KSTEP
COMMON/FRES/TABF
LEVEL 2,TABF
C HEADING
WRITE(6,6000)
6000 FORMAT(///20H RESULTS FROM WATES //)
5000 FORMAT(3I4)
5001 FORMAT(F10,0)
DO 10 I=M1,M2
IPMSQ(I)=(I*5)**2
10 CONTINUE
20 READ(5,5000)M0,MW1,MW2
C IF M0= ZERO RETURN TO MAIN PROGRAM
IF(M0)14,14,11
11 READ(5,5001)T
FMU=FLOAT(M0)
C CALCULATE THE WEIGHTS
R=1.0/FMU
DO 12 I=MW1,MW2
FI=FLOAT(I)
X=((1.0/FI)-R)**2)*I*FI
IF (X,EQ,0,0) GO TO 13
Y(I)=EXP(-X)
GO TO 12
13 Y(I)=1.0
12 CONTINUE
C SET WEIGHT OF NEUTRAL LAYER TO ONE
WF(M0)=1.0
I=M0+1
MW2S1= MW2-1
DO 70 J=M0,MW2S1
WF(I)=WF(I-1)*Y(I)
I=I+1
70 CONTINUE
I=M0-1
M0S1=M0-1
DO 71 J=MW1,M0S1
C WEIGHT FOR THE I TH LAYER IS IN WF(I)
WF(I)=WF(I+1)*Y(I)
I=I-1
71 CONTINUE
C APPLY WEIGHTS AND SUM CONTRIBUTIONS FROM REQUIRED LAYERS;RESULT IN AW
DO 15 L=1,KOUNT
AW=0.0
DO 16 MC=MW1,MW2
F=FLOAT(IPMSQ(MC))
BW=TABF(MC,L)*F*WF(MC)
AW=AW+BW
16 CONTINUE
C PUT RESULT OF SUMMATION INTO RES(L)
RES(L)=AW
--

```

```

15 CONTINUE
C OUTPUT RESULTS
  WRITE(6,6001)KR,LR,MW1,MW2,MO,T
C HEADINGS
6001 FORMAT(/25H PROFILE OF REFLECTION  0,11,11/
17H LAYERS,14,3H TO,14,11H CONSIDERED/
216H NEUTRAL LAYER =,13,5X,4H T =,F8.2/)
  RL=KMIN
  DO 19 L=1,KOUNT
  WRITE(6,6002)RL,RES(L)
6002 FORMAT(3H K=,F7.4,5X,F15.4)
  RL=RL+KSTEP
19 CONTINUE
  GO TO 20
14 CONTINUE
  RETURN
  END
  SUBROUTINE RESSJO(X,PHI,U0,V0)
C OXLIB 1900 LIBRARY PROGRAM
  IF(X,NE,0.0) GO TO 10
  U0=1.0
  V0=0.0
  RETURN
10 N=1
  IF(PHI,LT,0.0) N=-1
  ARG=ABS(PHI)
  IF(ARG,GE,3.14159265358979) ARG=ARG-3.14159265358979
  IF(X,GE,10.0) GO TO 11
  X1=X/2.0
  ZARG=ARG+ARG
  FAC=1.0
  DO 21 K=1,100
  FAC=FAC*X1/FLOAT(K)
  IF(ABS(FAC),LT,1.0E-10) GO TO 25
21 CONTINUE
  K=100
25 FK=FLOAT(K)
  U0=FAC*FAC*COS(FK*ZARG)
  V0=FAC*FAC*SIN(FK*ZARG)
  J=MOD(K,2)
  IF(J,EQ,0) GO TO 26
  U0=-U0
  V0=-V0
26 M=K
  DO 22 L=2,M
  K=K-1
  FAX=FAC*FLOAT(K+1)/X1
  FAX=FAC*FAC
  J=MOD(K,2)
  IF(J,EQ,0) GO TO 23
  FAX=-FAX
23 FK=FLOAT(K)
  U0=U0+FAX*COS(FK*ZARG)
  V0=V0+FAX*SIN(FK*ZARG)
22 CONTINUE
  U0=U0+1.0
  GO TO 12
11 C=SQRT(2.0/(X*3.14159265358979))
  A=C*COS(ARG/2.0)
  B=-C*SIN(ARG/2.0)
  C=COS(-3.14159265358979/4.0)
  S=SIN(-3.14159265358979/4.0)
  CA=COS(ARG)*X
  SA=SIN(ARG)*X
  CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
  CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S

```

```

SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
P=(5,0*5,0)/(2,0*2,0**6,0*X**2,0)
Q=1,0/(2,0*2,0**6,0*X**2,0)
P1=P
Q1=Q
DO 1 K=2,100
P=P*(FLOAT(4*K-1)*FLOAT(4*K-1)*FLOAT(4*K-3)*FLOAT(4*K-3))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
Q=Q*(FLOAT(4*K-3)*FLOAT(4*K-3)*FLOAT(4*K-5)*FLOAT(4*K-5))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
IF((P.LT,1.0E-10),AND,(Q.LT,1.0E-10)) GO TO 2
IF((P.LE,P1),AND,(Q.LE,Q1)) GO TO 8
P=P1
Q=Q1
GO TO 9
8 P1=P
Q1=Q
1 CONTINUE
K=100
GO TO 2
9 K=K-1
2 Q=Q*FLOAT(2*K)*FLOAT(2**3)*X
J=MOD(K,2)
IF(J,EQ,0) GO TO 3
I=-1
GO TO 4
3 I=1
4 FI=FLOAT(I)
FK=FLOAT(K)
PR=FI*P*COS(2,0*FK*ARG)
PI=-FI*P*SIN(2,0*FK*ARG)
QR=FI*Q*COS(2,0*FK*ARG-ARG)
QI=-FI*Q*SIN(2,0*FK*ARG-ARG)
M=K
DO 5 L=2,M
K=K-1
P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
1(FLOAT(4*K+3)*FLOAT(4*K+3)*FLOAT(4*K+1)*FLOAT(4*K+1))
Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
1(FLOAT(4*K+1)*FLOAT(4*K+1)*FLOAT(4*K-1)*FLOAT(4*K-1))
J=MOD(K,2)
IF(J,EQ,0) GO TO 6
I=-1
GO TO 7
6 I=1
7 FI=FLOAT(I)
FK=FLOAT(K)
PR=PR+FI*P*COS(2,0*FK*ARG)
PI=PI-FI*P*SIN(2,0*FK*ARG)
QR=QR+FI*Q*COS(2,0*FK*ARG-ARG)
QI=QI-FI*Q*SIN(2,0*FK*ARG-ARG)
5 CONTINUE
PR=PR+1,0
U0=A*(PR*CR-PI*CI-QR*SR+QI*SI)-R*(PI*CR+PR*CI-QI*SR-QR*SI)
V0=A*(PI*CR+PR*CI-QI*SR-QR*SI)+R*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(N,EQ,1) GO TO 13
V0=-V0
13 RETURN
END
SUBROUTINE BESSJ1(X,PHI,U1,V1)
C OXLIB 1900 LIBRARY PROGRAM
IF(X,NE,0,0) GO TO 10
U1=0,0
V1=0,0
RETURN

```

```

10 N=1
IF(PHI,LT,0.0) N=-1
ARG=ABS(PHI)
IF(ARG,GE,3.14159265358979) ARG=ARG-3.14159265358979
IF(X,GE,10.0) GO TO 11
X1=X/2.0
ZARG=ARG+ARG
A=COS(ARG)
B=SIN(ARG)
FAC=1.0
DO 21 K=1,100
FAC=FAC*X1/FLOAT(K)
IF(ABS(FAC),LT,1.0E-10) GO TO 25
21 CONTINUE
K=100
25 FK=FLOAT(K)
U0=FAC*FAC*FLOAT(K)*COS(FK*ZARG)
V0=FAC*FAC*FLOAT(K)*SIN(FK*ZARG)
J=MOD(K,2)
IF(J,EQ,0) GO TO 26
U0=-U0
V0=-V0
26 M=K
DO 22 L=2,M
K=K-1
FAC=FAC*FLOAT(K+1)/X1
FAX=FAC*FAC
J=MOD(K,2)
IF(J,EQ,0) GO TO 23
FAX=-FAX
23 FK=FLOAT(K)
U0=U0+FAX*FLOAT(K)*COS(FK*ZARG)
V0=V0+FAX*FK*SIN(FK*ZARG)
22 CONTINUE
U0=U0/X1
V0=V0/X1
U1=-(U0*A+V0*B)
V1=U0*B-V0*A
GO TO 12
11 C=SQRT(2.0/(X*3.14159265358979))
A=C*COS(ARG/2.0)
B=-C*SIN(ARG/2.0)
C=COS(-3.14159265358979*0.75)
S=SIN(-3.14159265358979*0.75)
CA=COS(ARG)*X
SA=SIN(ARG)*X
CR=COS(CA)*COSH(SA)*C-SIN(CA)*COSH(SA)*S
CI=-SIN(CA)*SINH(SA)*C-COS(CA)*SINH(SA)*S
SR=SIN(CA)*COSH(SA)*C+COS(CA)*COSH(SA)*S
SI=COS(CA)*SINH(SA)*C-SIN(CA)*SINH(SA)*S
P=3.0*5.0/(2.0*2.0**6.0*X**2.0)
Q=5.0/(2.0*2.0**6.0*X**2.0)
P1=P
Q1=Q
DO 1 K=2,100
P=P*FLOAT(4-(4*K-1)*(4*K-1))*FLOAT(4-(4*K-3)*(4*K-3))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
Q=Q*FLOAT(4-(4*K-3)*(4*K-3))*FLOAT(4-(4*K-5)*(4*K-5))/
1(FLOAT(2*K)*FLOAT(2*K-1)*FLOAT(2**6)*(X**2))
IF((P,LT,1.0E-10),AND,(Q,LT,1.0E-10)) GO TO 2
IF((P,LE,P1),AND,(Q,LE,Q1)) GO TO 8
P=P1
Q=Q1
GO TO 9
8 P1=P
Q1=Q

```

```

1  CONTINUE
   K=100
   GO TO 2
9  K=K-1
2  Q=Q*FLOAT(2*K)*FLOAT(2**3)*X
   J=MOD(K,2)
   IF(J,EQ,0) GO TO 3
   I=1
   GO TO 4
3  I=1
4  FI=FLOAT(I)
   FK=FLOAT(K)
   PR=FI*P*COS(2.0*FK*ARG)
   PI=-FI*P*SIN(2.0*FK*ARG)
   QR=FI*Q*COS(2.0*FK*ARG-ARG)
   QI=-FI*Q*SIN(2.0*FK*ARG-ARG)
   M=K
   DO 5 L=2,M
   K=K-1
   P=P*(FLOAT(2*K+2)*FLOAT(2*K+1)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4-(4*K+3)*(4*K+3))*FLOAT(4-(4*K+1)*(4*K+1)))
   Q=Q*(FLOAT(2*K+1)*FLOAT(2*K)*FLOAT(2**6)*(X**2))/
1 (FLOAT(4-(4*K+1)*(4*K+1))*FLOAT(4-(4*K-1)*(4*K-1)))
   J=MOD(K,2)
   IF(J,EQ,0) GO TO 6
   I=1
   GO TO 7
6  I=-1
7  FI=FLOAT(I)
   FK=FLOAT(K)
   PR=PR+FI*P*COS(2.0*FK*ARG)
   PI=PI-FI*P*SIN(2.0*FK*ARG)
   QR=QR+FI*Q*COS(2.0*FK*ARG-ARG)
   QI=QI-FI*Q*SIN(2.0*FK*ARG-ARG)
5  CONTINUE
   PR=PR+1.0
   U1=A*(PR*CR-PI*CI-QR*SR+QI*SI)-B*(PI*CR+PR*CI-QI*SR-QR*SI)
   V1=A*(PI*CR+PR*CI-QI*SR-QR*SI)+B*(PR*CR-PI*CI-QR*SR+QI*SI)
12 IF(ABS(PHI),LT,3.14159265358979) GO TO 13
   U1=-U1
   V1=-V1
13 IF(N,EQ,-1) V1=-V1
   RETURN
   END
   SUBROUTINE BESSJN(X,PHI,U,V,N)
   DIMENSION U(2),V(2)
   IF(X,NE,0.0) GO TO 30
   U(1)=1.0
   V(1)=0.0
   DO 31 I=1,N
   U(I+1)=0.0
   V(I+1)=0.0
31 CONTINUE
   RETURN
30 NN=1
   IF(PHI,LT,0.0) NN=-1
   ARG=ABS(PHI)
   IF(ARG,GE,3.14159265358979) ARG=ARG-3.14159265358979
   FN=FLOAT(N)
   IF(X,LE,FN) GO TO 1
   CALL BESSJ0(X,ARG,U(1),V(1))
   IF(N,LT,1) GO TO 20
   CALL BESSJ1(X,ARG,U(2),V(2))
   IF(N,LT,2) GO TO 20
   DO 10 I=2,N
   U(I+1)=(2.0*FLOAT(I-1)*U(I)*COS(ARG)+2.0*FLOAT(I-1)*V(I)*

```

```

1 SIN*(ARG))/X=U(I-1)
V(I+1)=(2.0*FLOAT(I-1)*V(I)*COS (ARG)-2.0*FLOAT(I-1)*U(I)*
1 SIN (ARG))/X-V(I-1)
10 CONTINUE
GO TO 20
1 N1=N+1
IX=IFIX(X)
K=IX+20
IF(K,LT,N) K=N
2 SCAR=1000000.0
SCAI=1000000.0
STRR=0.0000001
STRI=0.0000001
WAR=STRR
WAI=STRI
WBR=0.0
WBI=0.0
J=K+1
DO 3 I=1,K
J=J-1
WCR=(2.0*FLOAT(J)*WAR*COS (ARG)+2.0*FLOAT(J)*WAI*SIN (ARG))/X-WBR
WCI=(2.0*FLOAT(J)*WAI*COS (ARG)-2.0*FLOAT(J)*WAR*SIN (ARG))/X-WBI
WBR=WAR
WBI=WAI
WAR=WCR
WAI=WCI
IF((J-1),GT,N) GO TO 4
U(J)=WCR
V(J)=WCI
4 IF((ABS(WCR),LE,SCAR),AND,(ABS(WCI),LE,SCAI)) GO TO 3
WAR=WAR/SCAR
WBR=WBR/SCAR
STRR=STRR/SCAR
IF(J,GT,N1) GO TO 8
DO 6 L=J,N1
U(L)=U(L)/SCAR
6 CONTINUE
8 CONTINUE
WAI=WAI/SCAI
WBI=WBI/SCAI
STRI=STRI/SCAI
IF(J,GT,N1) GO TO 3
DO 9 L=J,N1
V(L)=V(L)/SCAI
9 CONTINUE
3 CONTINUE
CALL BESSJO(X,ARG,UL,VL)
ULAM=(UL*U(1)+VL*V(1))/(U(1)**2+V(1)**2)
VLAM=(VL*U(1)-UL*V(1))/(U(1)**2+V(1)**2)
IF((ABS (STRR*ULAM),LE,0.00000000001),AND,(ABS (STRI*VLAM),LE,
10.00000000001)) GO TO 5
K=K+10
GO TO 2
5 DO 7 L=1,N1
UU=U(L)
VV=V(L)
U(L)=UU*ULAM-VV*VLAM
V(L)=VV*ULAM+UU*VLAM
7 CONTINUE
20 IF(ABS(PHI),LT,3.14159265358979) GO TO 21
DO 22 I=1,N
K=MOD(I,2)
IF(K,EQ,0) GO TO 22
U(I+1)=-U(I+1)
V(I+1)=-V(I+1)
22 CONTINUE
23 IF(N,N1) GO TO 20

```

```

21 IF (X.NE.0) GO TO 23
    N1=N+1
    DO 24 I=1,N1
        V(I)=-V(I)
24 CONTINUE
23 RETURN
    END
    SUBROUTINE SPHEJN(X,U,V,N)
C OXLIB 1900 LIBRARY PROGRAM
    INTEGER A,B,C,D,E,F,G
    DIMENSION U(1000),V(1000)
    K=N+10
3    IF(K.GT.2000) GO TO 5
    FN3=0.0
    FN2=1.0
    J=K+N
    J2=K+N
    DO 1 J=1,J2
        FN1=FLOAT(2*(J-N)+1)*FN2/X=FN3
        IF(ABS(FN1).GT.1.0E20) GO TO 10
        GO TO 11
10    FN1=FN1/1.0E20
        FN2=FN2/1.0E20
        IF((J+1).GT.(2*N+1)) GO TO 11
        A=J+1
        B=2*N+1
        DO 12 L=A,B
            IF(L.LT.(N+1)) GO TO 13
            C=L-N
            U(C)=U(C)/1.0E20
            GO TO 12
13    D=N-L+1
            V(D)=V(D)/1.0E20
12 CONTINUE
11    IF(J.GT.(2*N+1)) GO TO 2
        IF(J.GT.N) GO TO 14
        E=N-J+1
        V(E)=FN1
        GO TO 2
14    F=J-N
        U(F)=FN1
2    FN3=FN2
    FN2=FN1
1    J=J-1
    U0=SIN(X)/X
    U1=SIN(X)/(X*X)-COS(X)/X
    P=U0/U(1)
    G=N+1
    DO 4 I=1,G
        U(I)=U(I)*P
    DO 6 I=1,N
        V(I)=V(I)*P
    K=K+10
    P=ABS(U(2)-U1)
    IF(P.GT.0.000000001) GO TO 3
5    RETURN
    END
    FUNCTION COSH(X)
    COSH=(EXP(X)+EXP(-X))/2.0
    RETURN
    END
    FUNCTION SINH(X)
    SINH=(EXP(X)-EXP(-X))/2.0
    RETURN
    END

```

C DATA CARDS

↑

#LISTING OF 1GEOL.ANDY1(1/) PRODUCED ON 14JAN74 AT 21.57.38

#OUTPUT BY LISTFILE IN 'GEOLOG.MOPCMS' ON 14JAN74 AT 22.37.55

DOCUMENT ANDY1

```

C**** PROGRAM WATES ****
MASTER WATES
REAL WFBM(100)
DIMENSION WF(100),Y(100),PMSQ(100),FMD(100),
1C(55,60)
DATA SPACE,STAR/1H ,1H*/
5001 FORMAT(F10.0)
5000 FORMAT(3I4)
C READ NEUTRAL LAYER, LAYERS TO BE CONSIDERED
13 READ(5,5000)M0,M1,M2
C IF M0 <= ZERO STOP
IF(M0)14,14,0
READ(5,5001)T
DO 10 I=M1,M2
FI=FLOAT(I)
C FOR ORTHO REPLACE 8.5 BY 5.0
PMSQ(I)=(8.5*FI)**2
10 CONTINUE
FMO=FLOAT(M0)
R=1./FMO
DO 12 I=M1,M2
FI=FLOAT(I)
X=((1./FI)-R)**2)*T*FI
Y(I)=EXP(-X)
12 CONTINUE
C SET WEIGHT OF NEUTRAL LAYER TO ONE
WF(M0)=1.0
I=M0+1
DO 70 J=M0,M2-1
WF(I)=WF(I-1)*Y(I)
I=I+1
70 CONTINUE
I=M0-1
DO 71 J=M1,M0-1
WF(I)=WF(I+1)*Y(I)
I=I-1
C WEIGHT OF I TH LAYER IS IN WF(I)
71 CONTINUE
DO 72 I=M1,M2
72 WFBM(I)=WF(I)*PMSQ(I)
C CALCULATE FREQUENCY DISTRIBUTION
C MC>M0
DO 17 MC=M0,M2-1
FMD(MC)=WF(MC)-WF(MC+1)
C SET UP GRAPHICAL OUTPUT
J=IFIX(FMD(MC)*1000.)
IF(J,GT.60) J=60
IF(J,EQ.0) J=1
DO 15 I=1,60
15 C(MC,I)=SPACE
C(MC,J)=STAR
17 CONTINUE
C CALCULATE FREQUENCY DISTRIBUTION AND SET UP GRAPHICAL OUTPUT
C MC<M0

```

[illegible]

APPENDIX B

<u>Specimen No.</u>	<u>Description</u>	<u>Locality</u>	<u>Source</u>	<u>Oxford Accession No.</u>
8/20F	Apple-green, splintery fibres (labelled ortho-chrysotile).	Unknown	1	-
9652) 3950) 3953)	greenish-yellow splintery fibres (labelled 'schweizerite')	Findeten glacier, nr. Zermatt	2	-
B-14) B-18) B-23) G-20) I-5)	dark-green serpentinite samples, cut by cross- fibre asbestos veins, with central partings of massive magnetite.	Shabani, Rhodesia do. do. do. do.	3 3 3 3 3	19537 19538 19539 19540 19541
AG 67-697 725 761 780 857 869 939 951 992 1013 1023 1044 1056 1130 1138 1148 1176 1185 1316	A series of drill core samples, dark green serpentinites, frequently cut by cross-fibre veins of chrysotile and brucite.	Jeffrey mine, Quebec	3	19542 19543 19544 19545 19546 19547 19548 19549 19550 19551 19552 19553 19554 19555 19556 19557 19558 19559 19560
SEP 5) 11) 1) 2)	Magnetic separates from commercial asbestos	Bell Mine, Canada) Black Lake, Canada) Havelock, Swaziland) Havelock, Swaziland)	5	- - - -

A number of fibre photographs were also examined -

<u>Specimen No.</u>	<u>Material</u>	<u>Locality</u>	<u>Source</u>
G 394	plate of magnesite from asbestos fibre bundle	Shabani, Rhodesia	3
G 435) G 218) G 632	chrysotile asbestos Povlen type clino- chrysotile	Shabani, Rhodesia do.	3 3
G 110	Povlen-type clino- chrysotile)	Unknown	4
G 136	Povlen-type ortho- chrysotile)		
G 148	Povlen-type clino- chrysotile (with) minor ortho-) chrysotile)		

Key to sources - 1 Department of Geology and Mineralogy, Oxford University.

2 Oxford University Museum.

3 Dr. E.J.W. Whittaker, Department of Geology and
Mineralogy, Oxford.

4 Dr. F.J. Wicks, Royal Ontario Museum.

5 Turner Brothers Asbestos Company.